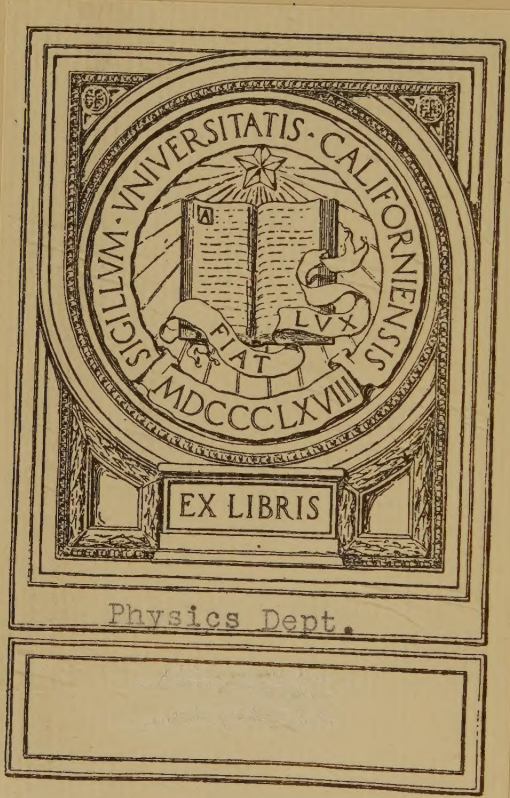
The George Fisher Baker
Non-Resident Lectureship in Chemistry
At Cornell University

UNIV OF CALIFORNIA



THE GEORGE FISHER BAKER
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VOLUME 8

The Wave Mechanics of Free Electrons

by

G. P. THOMSON

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The Wave Mechanics of Free Electrons

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G. P. THOMSON

PROFESSOR OF NATURAL PHILOSOPHY
UNIVERSITY OF ABERDEEN

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PREFACE

The following book represents the substance of lectures delivered at Cornell from October to December 1929, as part of my course as George Fisher Baker Non-Resident Lecturer in that University.

They are an attempt to state the principles and applications of the new wave mechanics, in so far as these concern electrons not forming part of an atom, using the minimum of mathematics. Most books on wave mechanics have been chiefly concerned with the spectroscopic side, but the experiments on electron diffraction are now sufficiently numerous to make it desirable that they should be collected together, and presented together with enough of the theory to make them understandable to the experimental physicist. This is the more important as it seems likely that the method of electron diffraction will find many applications in the next few years in physics, and perhaps also in investigations of commercial interest. I have kept strictly to the title and have not included any account of the recent attempts to detect waves accompanying systems of atomic or molecular size for, in spite of the interest and promise of these experiments, the situation is changing too quickly to make an account of much permanent value.

In conclusion I wish to express my most sincere thanks to the members of the Departments of Chemistry and Physics at Cornell who have combined to make my stay here an extraordinarily happy one, and especially to Professor Dennis for his unfailing kindness as a host, and for his care in providing me with everything that could be needed for laboratory or literary work.

For the work described in the last few pages I am much indebted to the assistance of Mr. H. R. Nelson of Cornell and Mr. J. D. McKay of Aberdeen.

Cornell University
January 31, 1930

INTRODUCTORY LECTURE

Waves and Particles

No one who has been so fortunate as to experience the magnificent reception—surpassing even the usual high standard of American hospitality—which you accord to the lecturers of this foundation could possibly begin his duties without a grateful recognition of such splendid treatment. To Mr. George Fisher Baker, the founder of this lectureship, and to Professor Dennis, to whom falls the arduous duty of administration, I want to express thanks which are out of all proportion to what can be expressed in these few words. This Foundation is of inestimable value to the men who are fortunate enough to hold it, in giving them an insight into the working of one of the most progressive universities of this country and an opportunity of becoming personally acquainted with a group of very distinguished men. I have a hard task in attempting to give anything approaching a fair return for these advantages, and I hope you will judge leniently my attempts to do so.

If I break this piece of chalk, then take each of the bits and break them, and so on, is there any theoretical limit to the process of comminution other than that imposed by the coarseness of mechanical appliances? This is a question which has occupied science since the twilight of its earliest dawn.

In the last three or four years opinions have altered as to the best answer to this question. During the first quarter of this century the answer to the question was quite definite. If the piece of chalk is continually broken and rebroken a time comes when the pieces are no longer merely smaller but become different in kind. This stage cannot be reached by mechanical breaking, but it can be reached by heat and suitable chemical action. The chalk has been broken into its atoms. In chalk there are three kinds; other

substances would yield other kinds, and, in all, chemists have distinguished ninety kinds from which all matter is made. These atoms are small. They bear about the same relation to a drop of water that a drop of water bears to the earth. But even here the limit has not been reached. Towards the end of the nineteenth century it had been found possible to break pieces off these atoms: for example, by the violent collision of other atoms. These pieces were always the same. They are called electrons and have now become almost an article of commerce, for they are the working material of the radio valve. The hot filament of the valve gives off electrons as water gives off steam, and the electric forces in the oscillating circuit control the motions of the electrons.

The older view of the electron is best expressed by regarding it as a tiny lump of electricity which had a little mass—less than a thousandth of that of a light atom—as a kind of secondary property of its charge. It was supposed to have a certain extremely minute size, but as a matter of fact the estimate of this size rested on purely theoretical arguments and no one had ever measured it. However, it soon became apparent that each atom contained electrons varying in number, from one each to nearly two hundred and fifty each, for different kinds of atoms. Thus it was reasonable to suppose that an electron was a good deal smaller than an atom.

Later on—it is difficult to give an exact date—it became clear that there was a second universal constituent and that this was the residue of a hydrogen atom when one electron—the only one—was removed. It has been called the proton. Every atom contains, in its normal state, an equal number of electrons and protons. The protons are much the heavier of the two, but they occupy only a very small region in the center of the atom called the nucleus. This region is so small that the combined nuclei of a man's body would form a barely visible speck. Since the nucleus also contains some electrons these apparently must be at least equally small, and we are left with a picture of matter as mostly emptiness. That such a view is not purely figurative has been shown in a striking manner

recently. It seems certain that some stars, known as "white dwarfs," are so dense that a cubic inch would weigh a ton. This is still nothing like the density of a nucleus, but it shows at least that an ordinary solid must have plenty of gaps if it can be compressed to such an extent. The picture of matter was thus essentially one of discontinuity. It consisted of a number of specks—of a whole number, for an electron or proton can not be split. It is a return to the earliest philosophy, for it was Pythagoras who taught that "all is number."

But there was another side of physics in which continuity was supreme. If you had asked the question: "How does one electron act on another?" the answer would have been "through stresses in the ether." Now the ether has had a long and checkered history. Ethers of a sort were common in early physics—rather too common. But the ether first acquired an assured status in the scientific world when it became clear that light had to be explained as *waves*. As this introduces the other half of the title of my lecture you will perhaps allow me to dwell on it in some detail.

The obvious thing about light is that it goes in straight lines—as can be seen if you watch light passing into a darkened room through a small hole and tracing out a path as it lights up the motes of dust. Now Newton said that a particle free from force goes in a straight line. It was natural to suppose that light consisted of a stream of particles shot out by the luminous object. Light can be reflected by mirrors and refracted by glass but, superficially at least, these effects can be explained as a rebounding of the light particles or their deflection by forces at the surface of the glass, as the case may be. Nevertheless, influential men such as the Dutch physicist Huygens suggested in the seventeenth century that light was a form of wave motion. Now sound is wave motion and every one knows that sound will go round corners. So will water waves. How can you explain the rectilinear propagation of light on this view? It is all a question of the wave-length. Even in sound a high-pitched note is not heard well round a corner. If the wave-length of light is

small enough rectilinear propagation is all right. Also light does bend very slightly. The really crucial test is what is called interference, the property by which two lights can produce darkness. A special form of this is to take a number of regular spaced wavelets, all derived from one wave. This gives a peculiarly marked effect. The effects of the combined wavelets are strongly concentrated in a few privileged directions and cancel everywhere else.

Light shows this phenomenon to a very marked extent. For example, in the case of the diffraction grating, light scattered from a large number of regularly spaced scratches on a glass or metal surface is found to be concentrated in a few directions, and this effect can be used to measure the wave-length of light with very great accuracy.

The ether was required to carry these light waves. At first it was thought of as a kind of jelly, and Lord Kelvin used immense mathematical skill in finding the very peculiar type of jelly which alone gives exact agreement with the experimental laws of light. Now Faraday long before had regarded electric and magnetic effects as stresses in a medium, and Maxwell showed that the same medium could do double duty, carry electric effects and transmit light. Hertz crowned the theory by actually producing waves by purely electromagnetic processes which had the velocity of light, and in fact were invisible light: "light" whose wave-lengths were to be measured in meters instead of thousandths of a millimeter as are those of the visible kind. I need hardly say that these waves are those now used in radio telegraphy. Later it was shown—not until 1913 indeed, but logically it comes in here—that X-rays are invisible light, on the other side as it were. Their wave-length is about 10,000 times shorter than that of ordinary light instead of millions of times longer. The way in which this was proved is of interest. To show interference well, one needs an apparatus so exactly shaped that the errors are smaller than the wave-length to be tested. Now X-ray wave-lengths are smaller than most atoms. It is impossible to shape an apparatus exact to an atom. Von Laue got over the difficulty in a very ingenious way. He remembered that in a crystal the atoms are arranged in regular order like

soldiers drawn up in close formation. The result is a series of lines like a diffraction grating and about the right distance apart. Actually it is a little more complicated because the atoms are arranged in a solid array while an ordinary grating is on a plane, but this does not really matter. The result of sending X-rays through a crystal is a diffraction pattern, and in this way the wave-lengths can be found.

So far, then, we have matter made of discontinuous particles, while the interaction is due to a continuous medium which can transmit waves. But now came the difficulties. I will take two selected ones which are enough to show their nature. When light is allowed to fall on a polished metal surface, electrons are thrown out from the metal. Since light is electromagnetic waves and electrons are electrical, it is not surprising that there should be an action of this kind, but the details are all wrong. The speed with which the electrons come out does not depend on the intensity of the light. They come out with just the same speed for the feeblest light as for the strongest, only there are fewer of them. Now if, for example, sea waves are breaking on the beach and rolling the pebbles about, the more violent the waves the farther the pebbles are thrown. If the water waves behaved like light, an almost calm sea would throw a few selected pebbles as violently as a great storm throws them all. This is obviously contrary to one's ordinary conception of waves, and it is equally at variance with the results of a complete mathematical treatment. Moreover, the energy with which the selected electrons appear is so great that they would take hours to absorb it from feeble light, while with even the feeblest light there is no detectable lag between switching on the light and the appearance of the electrons. Obviously something is wrong. Einstein suggested that the light contained units of energy or quanta which behaved practically like particles. When one collides with an electron it gives up its energy to the electron, which then can escape from the metal. All the quanta in a given kind of light are the same, the stronger the light the more numerous they are. The

energy of each quantum is the frequency of the light multiplied by a quantity h, which can be found by measuring the energy of electrons emitted by the light of known frequencies. This has been done by Professor Millikan. He finds $h = 6.55 \times 10^{-27}$. Now this is all very well for the photo-electric effect, as the above is called, but what about the diffraction grating? We have just decided that light must be waves and now it turns out to be particles instead, for it is essential for the explanation that the quanta should be so concentrated that one electron can catch a whole quantum. This is the famous photo-electric paradox.

Before I try to answer it, I will describe the other difficulty. Atoms can be made to emit light, and each atom emits its own characteristic wave-lengths. These are clearly a consequence of the structure of the particular atom, presumbably of the arrangement of its electrons. Now one theory, and one only, was found capable of explaining these wave-lengths even in general terms. This was the theory due to Neils Bohr according to which the electrons were supposed to move in orbits round the nucleus rather like planets round the sun. But in order to make the theory fit the facts, Bohr had to assume a behavior of the electrons which is quite contrary to ordinary dynamics, and curiously enough the same quantity h came in, though in quite a different way. The real trouble was not so much that the electrons obeyed laws different from those of Maxwell and Newton, but that they were not consistent about it. Some of the things they did required the old laws to explain them; others required a new and inconsistent set. Sometimes both had to be used in different parts of the same calculation. The position of a physicist investigating an atom was rather like that of a man trying to make sense of an account of a game which started as golf and suddenly for no apparent reason turned into tennis and then back to golf again. Worse still, as time went on it became clear that the electrons did not play fair even at the game they had for the moment chosen. The results were nearly right but not quite. The only

hint was that the quantity h came in whenever the atom chose to break the old rules, and this suggested a connection with the photo-electric paradox. The first really successful attempt to solve these difficulties is due to Prince L. de Broglie. He realized that the reason why the electron in the atom seemed to follow two different sets of rules at once was that it was behaving much more like a wave than a particle. Now if you think that you are reading an account of a game played with a ball, when really the reporter was writing about a swimming match, it is not to be wondered at if the report does not make good sense. It is perhaps surprising that the physicists made as much of it as they did. De Broglie's theory was a mathematical one based on relativity. He reached the conclusion that any moving particle would be accompanied by a wave, and he postulated that this wave controlled the motion of the particle. Instead of Newton's laws of motion (motion in a straight line, acceleration proportional to the force, and so on) this view gives a motion governed by waves. Of course Newton's laws are true in every-day life. This is because a very short wave is indistinguishable in behavior from a particle, and the scale of de Broglie's waves is given by h, which is a very small quantity. But according to his theory the smaller the particle the longer the wave. For an electron in an atom the wave is quite comparable with the size of the atom, and the behavior of the electron is greatly different from what you would expect of a particle. It has been found, in fact, that this theory when fully applied mathematically, as it has been by Schrödinger and others, brings order out of chaos in the explanation of the properties of atoms.

Further, it is capable of dealing with the photo-electric paradox. Granting that there are in fact quanta, or particles, in radiation, they will inevitably be accompanied by waves which will guide them. The quanta will appear where the waves are strong; where there are many quanta the light will be intense. In other words, the regions of brightness and darkness will be just those predicted on the wave theory. This way out had indeed been suggested

before. It turns the flank of the difficulty by saying that it is the natural way for a particle to behave. But if you accept this you must be prepared to take the consequences. A free electron, such as a cathode ray, should also be guided by waves and should also show diffraction. How could we hope to detect it if it did? Calculation shows that the wave-length of a free electron of manageable energy is of the same order as that of X-rays. Can we not use a method similar to that by which the waves of X-rays have been measured and take advantage of the regular structure of crystals?

Successful experiments on these lines have in fact been made by Dr. Davisson and Dr. Germer in this country and by myself and others in Scotland. In my own experiments a narrow beam of fast electrons, cathode rays in fact, pass through a very thin film of metal. The metal scatters the electrons and, since metals consist of a number of minute crystals, the scattering occurs predominantly in certain privileged directions, just as is the case with X-rays. Accordingly, if the electron strikes a photographic plate placed somewhere behind the thin film we should expect to get a pattern similar to that produced by X-rays of the same wave-length. This expectation is in fact realized. I have obtained these diffraction patterns from a considerable number of metals. In all cases the patterns are in exact agreement with what is to be expected if they are regarded as the result of diffraction of waves by the known crystal structure of the particular metal used (See Figs. 19-20). The patterns are in general formed of concentric rings just like the familiar Debye-Scherrer X-ray powder photographs. From the sizes of the rings it is possible to deduce the wave-length of the waves causing them, and I find in all cases absolute agreement with the theoretical expression due to de Broglie, $\lambda = h/mv$. Thus instead of being scattered irregularly by the metal, it appears that if the film is thin enough it will guide the electrons into the directions which would be taken up by waves diffracted from the crystal structure of the metal.

If you accept the experiments as showing that electrons behave as if guided by a train of waves, you will agree that

de Broglie's idea brings a remarkable simplification. Both electrons and light quanta are on the same footing as particles guided by waves. The difficulties of physics in the earlier years of this century were due to ignorance of this dual character. For some reason we had got hold of the wave aspect of light and the particle aspect of electrons, and were running each to the exclusion of the complementary view. It also explains the curiously confusing nature of the difficulties. If we had neglected, say, the wave aspect in each case, all the new facts would have pointed to waves. As it was, some pointed to particles and some, as we now know, to waves.

This dual aspect of things as waves and particles must be very fundamental in the world. There is little doubt that protons would show it also, though experimental proof has, so far, not been possible. There is even strong, though indirect, evidence that a completed atom has a wave as a whole as well as component waves for its individual electrons. One reason for regarding the duality as really fundamental is that it holds for such different things as electrons and quanta. For in spite of this one point of resemblance they are essentially different. The electron has electric charge and hence is influenced by electric and magnetic forces in a way that the quantum is not. The quantum always goes (*in vacuo*) with a speed of 300,000 kilometers a second. The electron can go with any speed, provided it is less than this. For equal wave-lengths the penetrating power is quite different. These differences make it all the more significant that they should both show the same curious duality. The new view is not by any means free from difficulties. To take the most obvious, many electrons form part of each of the atoms of a crystal, yet the experiments I have described essentially involve the idea that the wave of the moving electron is spread over a number of the atoms in the crystal. Have we proved that the part is greater than the whole? I think that even modern physics is not so paradoxical as this. It depends on what you mean by the size of an electron. We can measure the size of atoms in a fairly definite way by finding how

many can be packed into a given space of solid. It is rather like measuring the size of shot by counting how many will fill a cartridge case of known volume. Of course we have to allow for possible empty spaces between, but this can be done if we know how they are piled together, and in many cases we do. The sizes are not quite definite; they vary a little with circumstances, but this is not surprising. Suppose that you want to know the size of a tennis ball. It is easy enough to measure it to an accuracy which will satisfy the authorities at Wimbledon that it is legal, but if you were asked to give its diameter to a hundredth of an inch there would be difficulty. Are you going to measure it to the furthest-out hair of the felt? Obviously that is not a very important measurement; but where are you going to stop? There is no sharp edge. Here a rough measurement has a real and useful meaning, but if you try to make it precise beyond a certain point it can be done only by making some arbitrary convention, such as how hard the measuring instrument is to press. This is the case for the atom, but for the electron the size is even less definite. It has not even an approximate boundary, as far as our present knowledge goes. It is more like a gas which can expand to "fill" (in a sense) any vessel into which it is put, and yet can be compressed into a very small space. When an electron is part of an atom its waves curl round, as it were, on themselves until it occupies only the atom, and perhaps only a part of that. When it gets free from the atom as a cathode ray, or escapes from the filament of a valve, its waves can uncurl and expand indefinitely. I think, however, that in all cases one must consider it as also having a sort of center, even if this is only a mathematical point. Whenever an electron produces any detectable effect it does so as a particle, and it seems easiest to suppose that even when it is not producing an effect the particle is somewhere round. The best analogy I have been able to find for this view is a gossamer spider.

When this little animal is clinging to the stalk of a plant, it is a small solid object. When it wants to move it shoots out long filaments many times its own length. The

wind catches these and wafts it away. I regard the filaments as analogous to the waves which surround the electron, while the body of the spider is analogous to the central point. One can press the analogy further. If the wind carries the spider so that one of its filaments is caught in an obstacle, the spider will be swung around and its path deflected although its body has not hit anything solid. In just the same way with the electron, if its waves pass over an obstacle, say an atom, the direction is modified and this modification is transmitted back through the wave system to the electron itself. If we suppose that the electron is constrained always to move in a way determined by the waves in its immediate neighborhood, the motion of the electron itself will thus be modified. The waves thus act as a kind of intermediary between the disturbing objects and the electron itself. The electron goes where the waves in its immediate neighborhood carry it, just as the spider is pulled by the parts of the filaments which are actually attached to it. But the form of the waves, near the electron, is determined by events at a distance, whose effects are propagated through space in the form of waves.

A question that inevitably arises is: What is the medium which transmits electron waves? I am sorry that I can give no entirely satisfactory answer. For the first time, physics is faced with waves in empty space which do not fit into the ordinary series of ether vibrations. All the ether vibrations differ only in wave-length; if the wave-length is given, the kind of "light" is fixed. The electron waves have varying wave-lengths depending on the speed of the electron, but they usually fall in a region of wave-lengths which is already appropriated by X-rays. As we have seen, they are certainly not the same as X-rays. One must suppose some other medium, or at least that the ordinary ether is in some way profoundly modified by the presence of the electron. It is possible that they are waves in a "subether." But it is not a very attractive idea to have two ethers filling space, especially as the waves of protons—if they exist—would demand yet a third. Space is becoming overcrowded. Other suggestions are to regard the waves as a kind of

mathematical abstraction, a sort of ghost waves. The whole question is getting very metaphysical. Perhaps a simple physicist may be content as long as the waves do their job of guiding the electron, and it is possible that, after all, the question will ultimately be seen to be meaningless. Whatever the medium is, the new wave conception has altered the view we take of the best answers to the question with which I began this lecture. Matter is still supposed made of discrete units, but instead of these units moving according to laws which concern them alone, as did the laws of Newtonian dynamics, we have had to introduce laws based on waves. Now a wave is essentially a continuous thing, even if the continuity is only mathematical. It is spread through space, not divided into little lumps. So although the older belief in the discontinuity of matter still holds, it has lost some of its rigidity; continuity has crept in by the back door.

The idea of ether has also changed. The sole function left it is to guide the quanta; they do the work. The picture of light as waves breaking on a shore of matter and thus disturbing it, is replaced by one of a stream of bullets which affect only the particular objects which they hit. The bullets, it is true, do not move quite as ordinary bullets would; they are directed by the waves, but all the effects are bullet effects, not wave effects.

We have seen that Newtonian mechanics needs modification; that it is a simplification which is permissable only when the wave-length is very small. This, of course, does not detract from its practical value in every-day life and in astronomy, nor from our estimate of the genius which gave it a form which has satisfied two and a half centuries. On the contrary, the new developments, as far as they concern light, which I have tried to explain to you at such length, are much better expressed in the words of Newton's Optics:

> Those that are averse from assenting to any new discoveries but such as they can explain by an hypothesis, may for the present suppose, that as stones by falling upon water put the water into an undulatory

motion, and all bodies by percussion excite vibrations in the Air; so the Rays of Light excite vibrations in the refracting Medium or Substance . . . that the vibrations thus excited are propagated in the refracting or reflecting Medium or Substance, much after the manner that vibrations are propagated in the Air for causing Sound, and move faster than the Rays so as to overtake them . . . and that every Ray is successively disposed to be easily reflected or easily transmitted by every vibration which overtakes it. But whether this Hypothesis be true or false I do not here consider.

After being regarded for generations as an artificial attempt to save a dying theory, we have proved this "guess" of Newton's to be a supreme example of the intuition of genius.

CHAPTER I

General Theory of Waves

In this chapter will be given some of the fundamental properties of wave motion which will be needed later on. The treatment of wave motion in elementary textbooks of physics, and even in some that are fairly advanced, is usually so simplified that points of considerable importance for our purposes fail to appear at all.

It is not an easy matter to define wave motion with generality and precision. Even the mathematical definition of it as the solution of a differential equation is open to objection, for there are several modifications of the usual form which are equally well entitled to be considered wave equations. It seems best to start from familiar instances and show how the conception of what constitutes a wave can be gradually broadened. Fundamentally a wave is an effect which has a definite value at a definite place and time, but in general varies continuously from place to place and from time to time. In one specially important and simple type of wave the variation with time is the same everywhere, and is simple harmonic. Such a wave is called a monochromatic wave. At a single point the effect

$$\psi = a\sin(nt+\delta) \qquad (1)$$

where a is the amplitude, $n/2\pi$ is the frequency ($2\pi/n$ is the period) and $nt+\delta$ will be called the phase. (In some books this name is applied to δ alone). The simplest wave of this type is the plane wave of constant amplitude $\psi = a\sin(nt \pm 2\pi x/\lambda)$ where λ is called the wave-length. Another form is the spherical wave

$$\psi = \frac{c}{r}\sin(nt \pm 2\pi r/\lambda) \qquad (2)$$

It should be noted that a monochromatic wave implies the existence of the motion for all values of t from $-\infty$ to

$+\infty$, thus a wave which has a beginning or an end cannot be strictly monochromatic.

The two cases of waves we have quoted come under the general form

$$\psi = a_{xyz}\sin(nt-\phi_{xyz}) \qquad (3)$$

where a and ϕ are functions of the space, but not of the time, co-ordinates. Though this expression includes forms of motion which are not generally classed as waves, it is of interest to examine some general properties of it. We define a wave front as a surface over which ϕ is constant. It is thus a surface of constant phase at a given time. Consider a surface which moves so as always to be a surface

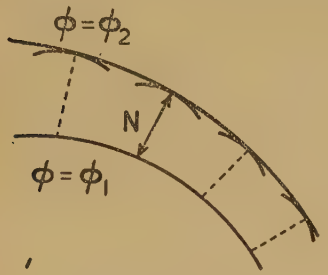


FIG. 1

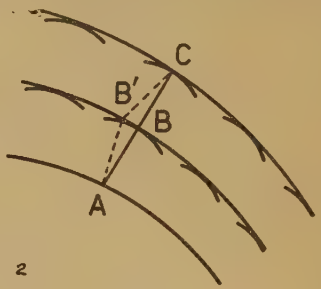


FIG. 2

of the same constant phase (Fig. 1), *i.e.* such that $nt-\phi_{xyz} = c$. As t changes ϕ must do so too, thus the surface moves. If $\phi = \phi_1$, $\phi = \phi_2$, represent two adjacent positions at times t_1 and t_2, then $nt_1-\phi_1 = nt_2-\phi_2$, and if N is the length of the common normal, the speed with which the surface ϕ moves normal to itself is $\underset{t_1\to t_2}{\mathrm{Lt}} \frac{N}{t_1-t_2} = \underset{\phi_1\to\phi_2}{\mathrm{Lt}} \frac{Nn}{\phi_1-\phi_2}$

$= \frac{n}{|\mathrm{grad}\ \phi|}$. We will call this speed "v", the phase speed,

$$v = \frac{n}{\left[\left(\frac{\partial\phi}{\partial x}\right)^2+\left(\frac{\partial\phi}{\partial y}\right)^2+\left(\frac{\partial\phi}{\partial z}\right)^2\right]^{\frac{1}{2}}} \qquad (4)$$

Since ϕ is a function of the co-ordinates, v will also in general be so. If v were known this method would make it possible to determine the way in which a wave front

progresses. The well-known Huygens construction involves this idea with the additional assumption that v is constant. This last assumption is quite unjustified even if the medium is everywhere the same, for v has been arrived at by a kinematic, not a dynamic argument. However for the two simple types of waves quoted above it is easy to see that $v = n\lambda/2\pi$ and is therefore constant. Though generally regarded as a wave theorem Huygens' construction (for isotropic media) implies nothing not already given by geometrical optics. It is well known that these can be summed up in Fermat's principle that the path of a ray is such that the time taken for the light to go along it is a maximum or minimum as compared with any adjacent possible path between the two points. Since the Huygens wavelets represent the distances travelled by the light in equal times, a line drawn everywhere normal to their envelope will have the Fermat property, and be a geometrical ray, *ABC* and *AB'C* (Fig. 2), differing only to the second order of small quantities. Thus Huygens wave fronts are no more than a set of surfaces orthogonal to the geometrical rays.

It is best at this point to start a different line of argument. Both the typical expressions for ψ which we have given satisfy a differential equation of the form

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} = \frac{1}{V^2}\frac{d^2\psi}{dt^2}, \qquad (5)$$

where the wave velocity V is written for $n\lambda/2\pi$. This equation is often spoken of as the wave equation *par excellence* though, as we shall see, other forms are also used. If V is a constant, the simplest case, all plane waves of constant amplitude are propagated with equal speed, and it is easy to see that for such waves $v = V$. The same is true for the type of spherical waves considered above.

If we agree to consider any solution of the above equation as a wave, it is at once seen that such waves can be superposed. For if ψ_1,ψ_2 are two solutions $\psi_1+\psi_2$ is also a solution. This principle of superposition is not exactly true for real waves of finite amplitude in material media; in water waves it ceases to be true for waves of

quite moderate amplitude compared with their length, and even for sound ceases to hold for violent sounds, such as those due to explosions. There is, however, no evidence at present to suggest that it fails for any of the types of light wave or for the electron waves with which this book chiefly deals, and the agreement with experiment of theoretical calculations based on this assumption is extremely exact in the case of visible light. We must however be prepared to consider V as a function of the co-ordinates and even sometimes of the time. V is known as the wave velocity. When V is a constant a mathematical theorem due to Kirchoff[1] shows that if ψ satisfies differential equation (5) the value of ψ at any place and time, $\psi(x_0,y_0,z_0, t_0)$, is determined by the values of ψ taken over a closed surface surrounding x_0,y_0,z_0, and calculated at a time t_0-r/V, where r is the distance from the element of the surface to the point x_0,y_0,z_0, together with the values of

FIG. 3

$$\frac{\partial\psi(x,y,z,t_0-r/V)}{\partial x}, \quad \frac{\partial\psi(x,y,z,t_0-r/V)}{\partial y}, \quad \frac{\partial\psi(x,y,z,t_0-r/V)}{\partial z},$$

over the same surface. The surface must be drawn so as not to contain any singularities such as sources or sinks of energy. Physically this theorem means that the equation represents a motion which is propagated everywhere with speed V, so that the condition at a point is determined by the conditions at distant points at an earlier time, the time interval being that required for the effect to travel between the two points with speed V. This theorem is the mathematical justification for the Fresnel treatment of diffraction problems, but it is not a complete justification. The argument runs thus. The effect at a point P (Fig. 3) can be calculated from the known effects over the surface

[1] For a proof of this theorem see Drude's *Optics*, p. 179 (Longmans, Green & Co., New York, 1913).

ABC, which is supposed continued to infinity so as to surround *P* with a hemisphere at infinity. The effect of the hemisphere is neglected because the phases of the disturbance at points on it will be distributed at random and will cancel. Thus the effect at *P* appears as an integral taken over the surface *ABC*. The integral actually is

$$\int \frac{dS}{4\pi}\left[\cos(n,r)\frac{\partial}{\partial r}\left(\frac{\psi(t-r/c)}{r}\right)-\frac{1}{r}\frac{\partial}{\partial n}\psi(t-r/c)\right],$$

where n is the normal to the surface *ABC*.

If *ABC* is a plane (it is to be remembered that it is an arbitrary surface, not even necessarily a wave front), and if the wave system is one of plane waves parallel to it, given by $\psi = a\sin(nt-2\pi x/\lambda)$, the integrand for large values of r becomes $-\frac{a}{2\lambda r}(1+\cos\theta)\sin(nt-\frac{2\pi r}{\lambda})$ where θ is the angle between r and the normal to the wave front. Fresnel's diffraction theory is equivalent to assuming that if part of the wave is blocked by an obstacle in the plane *ABC*, the remainder will continue to produce an effect at *P* corresponding to the above expression, so that the total effect is obtained by integrating the expression over the part of *ABC* which has not been blocked out. This assumption is in fact inexact; it would imply a displacement which changes discontinuously near the screen and so is not a solution of the original differential equation. It is thus inconsistent with the original starting point of the argument. It appears however from the few cases in which an exact solution of the wave equation with suitable boundary conditions is possible, that the Fresnel approximation is extremely close except within a few wave-lengths of the screen. As is well known, it is in excellent agreement with the experiments.

A similar differential equation can be used as the definition of waves when V is a function of x,y,z. In such a case Kirchoff's theorem will break down, but unless V varies appreciably in a wave-length the same general idea of propagation from point to point will continue to hold.

The form $\psi = a\sin(nt-\phi)$ is equivalent to $\psi = ae^{i(nt-\phi)}$ where the imaginary part is to be taken at the end. Substituting in $\nabla^2\psi = \frac{1}{V^2}\frac{\partial^2\psi}{\partial t^2}$ and equating real and imaginary parts we find

$$a\nabla^2\phi + 2\sum_{xyz}\frac{\partial a}{\partial x}\frac{\partial\phi}{\partial x} = 0 \qquad (6)$$

and

$$\nabla^2 a - a\sum_{xyz}\left(\frac{\partial\phi}{\partial x}\right)^2 = -\frac{n^2}{V^2 a} \qquad (7)$$

If a is constant these reduce to $\nabla^2\phi = 0$ and $V^2 = \frac{n^2}{\sum_{xyz}\left(\frac{\partial\phi}{\partial x}\right)^2}$, *i.e.* $V = v$. In such a case we can write $\psi = c\sin n\left(t - \int\frac{dr}{V}\right)$ since $v = \frac{n}{\partial\phi/\partial r}$, where r is the normal to the wave front. Thus ψ is fully determined by conditions along a line. This line, which is always normal to the wave front, may be called a ray and the circumstances of the motion may be expressed in terms of geometrical optics, successive wave fronts being determined by Huygens' construction. This will occur even when a is variable if $\nabla^2 a = 0$, an instance being the spherical wave for which $a = 1/r$. We see, then, that in order that the waves should contain information which could not be obtained by geometrical optics, it is necessary that their amplitude should be variable and should not satisfy Laplace's equation. If a is known, the equation $a\nabla^2\phi + 2\sum_{xyz}\frac{\partial a}{\partial x}\cdot\frac{\partial\phi}{\partial x} = 0$ is a restriction on ϕ showing that the original assumption $\psi = a\sin(nt-\phi)$ is too general to be a solution of the differential equation. Notice that this condition does not contain V.

In considering the difference between V and v it should be remembered that the former is regarded as a physical property of the medium at the given time and place, while the latter is defined from the kinematics of an assumed wave and may be different for different waves at a given place, even if the frequency is kept constant.

Still assuming that the waves are solutions of

$$\nabla^2\psi = \frac{1}{V^2}\cdot\frac{\partial^2\psi}{\partial t^2},$$

two important cases arise according as V does or does not depend upon the frequency. As is well known, in many cases waves travel at speeds which vary with the frequency of the waves. This is so for water waves, and for light waves in a dispersive medium. We shall see that it is true also for electron waves.

Now the most general effect at any given place can be represented over a limited period of time by a series of sines and cosines—a Fourier series. Thus

$$\psi(t) = a_1\sin\frac{t\pi}{T} + a_2\sin\frac{2t\pi}{T} + \ldots a_n\sin\frac{nt\pi}{T} + \ldots +$$

$$b_0 + b_1\cos\frac{t\pi}{T} + b_2\cos\frac{2t\pi}{T} + \ldots b_n\cos\frac{nt\pi}{T},$$

where the expression is valid between $t = -T$ and $t = T$. If the time interval is made very large, from $-\infty$ to $+\infty$, the series passes into a Fourier integral which may be regarded as meaning that the effect can be regarded as the sum of a number of vibrations of all possible periods. The amplitude corresponding to any period, or rather to any infinitesimal range of periods, depends on the form of the function of the time which the integral is to represent. The integral may be written

$$\psi(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\psi(\kappa)d\kappa\int_{-\infty}^{\infty}\cos\alpha(\kappa-t)d\alpha,$$

in which the coefficient of $\sin\alpha t$, for example, is $\frac{1}{2\pi}\int_{-\infty}^{\infty}\psi(\kappa)\sin\alpha\kappa\,.d\kappa$. If V is constant a plane wave of any form can be propagated unchanged. For consider $\psi = \int_{-\infty}^{\infty}f(\lambda)\frac{\sin 2\pi}{\lambda}(x-Vt)d\lambda$; it satisfies the differential Equation (5), when $t = 0$ it represents the most general expression in x. If x and t increase so that $x-Vt$ is constant the integral is unchanged, hence if the origin of x is shifted to the right with velocity V the expression is a

function of x only. It is thus a disturbance moving with velocity V without change of form. Clearly this argument only holds if V is independent of λ, or in other words of the frequency.

It should be noticed that this constancy of form has only been proved for infinite plane waves. If, for example, there is diffraction, the waves of different wave-length will be treated differently and there will be more or less sorting out of the waves. This is of course what happens when white light is analyzed by a diffraction-grating.

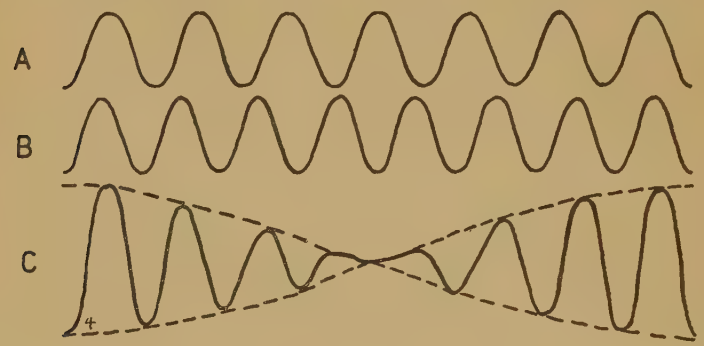


FIG. 4

When V is a function of n, even a plane wave will not travel unchanged unless it happens to be of simple sine curve form or in one or two other quite exceptional cases. The medium in this case is said to be dispersive and it is important to consider the kind of changes which occur in waves transmitted in such a medium.

Take first a disturbance represented by the sum of two simple waves A and B of equal amplitude and nearly the same frequency (Fig. 4). We have

$$\psi = a\sin(nt-2\pi x/\lambda) + a\sin(n't-2\pi x/\lambda')$$
$$= 2a\sin(nt-2\pi x/\lambda)\cos\left\{t\frac{n-n'}{2} - \pi x(1/\lambda-1/\lambda')\right\}$$

approximately. This is the well-known expression for "beats" in sound and can be regarded as representing a wave C (Fig. 4) whose intensity slowly varies. The in-

tensity factor is in form a wave, and the velocity of this "wave of amplitude" is $\frac{n-n'}{2\pi/\lambda-2\pi/\lambda'} = -\lambda^2/2\pi\cdot\frac{dn}{d\lambda}$ in the limit. Since $n/2\pi = V/\lambda$ this can also be written $V-\lambda\frac{dV}{d\lambda}$. If the phase is written $nt-mx$ it assumes the simple form dn/dm. This is known as the group velocity and plays a very important part in the study of waves in a dispersive medium. We shall denote it by U.

The two waves of nearly the same wave-length form what is called a group and the group velocity is the velocity with which a peculiarity associated with the group, such as a maximum of amplitude, will advance. The group velocity may be quite different from the wave velocity. For example in the case of gravity waves on the surface of deep water it is just half the wave velocity. A rather more general kind of group is one formed of waves whose wave-length varies continuously over a small range of wave-length $\delta\lambda$. Such a group has only one maximum of amplitude when all the component waves are in phase, but if $\delta\lambda$ is very small the amplitude will vary very slowly on both sides of this point. For many approximate calculations it is more convenient to regard an irregular disturbance as composed of a large number of elementary groups, than as analyzed into its primary Fourier components. Thus, consider the spreading of a splash over the surface of water. If surface tension is neglected

$$V=(g\lambda/2\pi)^{\frac{1}{2}},\quad U=\tfrac{1}{2}V.$$

Take the Fourier analysis first. The irregular splash can be analyzed into Fourier components, to each of which corresponds a wave of different wave-length. Initially these waves are all in phase at the origin of the splash, but get out of step and cancel farther out. As time goes on the waves are propagated with different velocities. At any given place and time most of them have phases distributed at random and so cancel, but there will be a certain range of wave-lengths which are nearly in phase, because the initial "out-of-stepness" due to their varying

wave-length is just balanced by that due to their varying speed. But these are precisely the waves whose group velocity has carried them from the origin, where all were initially in phase, to the point in question at the given time. Thus the predominant effect is due to a certain group. The condition for stationary phase at a distance x and time t is clearly

$$tn - \frac{2\pi x}{\lambda} = tn' - \frac{2\pi x}{\lambda'} \text{ or } x/t = \text{Lt}\, \frac{n - n'}{\frac{2\pi}{\lambda} - \frac{2\pi}{\lambda'}} = \text{U}.$$

Thus $x = \text{U}t$, and we can find what group will be the prominent one at a given place and time by finding the velocity x/t with which it must have moved and using the expression $\text{U} = \frac{1}{2}(g\lambda/2\pi)^{\frac{1}{2}}$ to find λ. Such a treatment is of course approximate only; a truly elementary group, for which $\delta\lambda$ is infinitesimal, is infinite in length, but the treatment becomes more and more exact the larger x and t.

The actual wave crests move with the speed V, twice as fast as the group and their motion is an accelerated one for they are continually getting to places where the predominant wave-length of the group is longer, and both wave and group speed is greater.

The idea has been expressed mathematically by Lord Kelvin. In an integral of the type $\psi = \frac{1}{2\pi}\int_0^\infty f(m)e^{i(nt - mx)}\, dm$ where $f(m)$ varies slowly with m, the only important parts are those for which the phases of the exponentials agree, otherwise they vary nearly evenly from 0 to 2π and the terms corresponding to them cancel out. This means that $nt - mx$ is stationary for varying m, therefore $tdn/dm - x = 0$. But $\text{U} = dn/dm$ hence $\text{U} = x/t$ as before, and the groups move out with their group velocity. Further analysis shows that $\psi = \frac{f(m)\cos(nt - mx \pm \pi/4)}{\sqrt{|2\pi t \,.\, d^2n/dm^2|}}$.[1] The wave-length and period at a place are found from the

[1] Lamb, *Hydrodynamics* (Cambridge Univ. Press, 1924), p. 373.

space and time variations of the phase of the predominant group. Since

$$\frac{\partial}{\partial x}(nt - mx) = (t.dn/dm - x)dm/dx - m = 0 - m = -m,$$

and

$$\frac{\partial}{\partial t}(nt - mx) = n + (t.dn/dm - x)dm/dt = n,$$

it follows that the wave-length and period in the neighborhood of x at time t are $2\pi/m$ and $2\pi/n$, respectively.

We follow a particular wave, *e.g.* a crest, if $dx/dt = V = 2U = 2x/t$, that is if t^2/x is constant. Thus the motion of a wave crest shows uniform acceleration $x = t^2/c$.

The longer the motion continues the more nearly monochromatic the groups become, and the greater is the number of waves which succeed each other with less than some assigned change in wave-length.

CHAPTER II

De Broglie's Wave Mechanics

Mention has been made in the Introductory Lecture of the difficulties with which physics was faced in the first quarter of the century. The chief were: the difficulty of reconciling the photo-electric effect with the facts of interference; the arbitrary nature of the hypotheses required to give Planck's equation; and a growing conviction that, in spite of its great successes, the Bohr-Sommerfeld theory was inadequate to account for some of the spectroscopic results even with the additional hypothesis of electronic spin.

The publication of L. de Broglie's doctor's thesis[1] in 1924, and a paper by him in the *Philosophical Magazine* of the same year, were the first signs of a satisfactory way out of these difficulties.[2] De Broglie started from the idea that Einstein's equation $E = h\nu$ represents a fundamental relation between energy and frequency. By the theory of relativity a particle of resting mass m_0 has associated with it energy m_0c^2, where c is the velocity of light, and should therefore have an inherent frequency $\nu_0 = \frac{m_0c^2}{h}$. De Broglie regarded this as the frequency of a pulsation in the space surrounding the particle. We may write this as $\psi = a\sin 2\pi\nu_0 t_0$, leaving it for the moment an open question whether a is a function of the co-ordinates or not; t_0 is the time measured for an observer at rest with the particle. Now suppose the particle to move with velocity u along the x axis. We find on applying the Lorentz transformation

$$\psi = a\sin\frac{2\pi\nu_0}{(1-u^2/c^2)^{\frac{1}{2}}}\left(t-\frac{ux}{c^2}\right)$$

where t and x refer to the new axes. This expression is a wave

[1] L. de Broglie, *Dissertation* (Masson, Paris, 1924).

[2] De Broglie, *Phil. Mag.*, **47**, 446 (1924); *Ann. phys.*, **3**, 22 (1925); De Broglie and Brillouin, *Wave Mechanics* (Blackie, London, 1928).

if a is a constant and in some cases when it is not (p.20). The frequency is $= \nu = \dfrac{\nu_0}{(1-u^2/c^2)^{\frac{1}{2}}} \dfrac{m_0c^2}{h(1-u^2/c^2)^{\frac{1}{2}}} = \dfrac{mc^2}{h}$, where m is the apparent mass relative to the new axes, thus the relation $E = h\nu$ remains true. We may write $\psi = a \sin 2\pi\nu(t-x/V)$ where $V = c^2/u$ is the wave velocity. It is clearly greater than the velocity of light. This is apparently contradictory to the principle of relativity that no signal can be transmitted faster than light. The contradiction is only apparent, however, for the transmission of a signal by waves is analogous to the case of a sudden disturbance of water considered in the last chapter, and we have seen that it is the group velocity which determines how fast the disturbance of a given wave-length will spread. Let us find the group velocity; it is the relation between x and t when the phase is stationary for varying frequency, *i.e.* varying u.

Thus $$t\cdot\frac{d\beta}{du} - \frac{x}{c^2}\frac{d(\beta u)}{du} = 0, \quad \beta = \frac{1}{(1-u^2/c^2)^{\frac{1}{2}}}.$$

The group velocity

$$U = x/t = \frac{c^2\cdot d\beta/du}{\beta + u\,.\,d\beta/du}, \quad \text{but} \quad d\beta/du = \frac{\beta u}{c^2-u^2},$$

therefore $$U = \frac{c^2u/(c^2-u^2)}{1+u^2/(c^2-u^2)} = u.$$

The group velocity is thus the speed of the particle, which of course never exceeds that of light. The wave-length λ of the plane wave is given by $\lambda = V/\nu = c^2/u\nu = \dfrac{mc^2}{mu\nu} = h/mu$, where m is the apparent mass. Since mu is the momentum, even on the relativity mechanics, λ is $h/$(momentum). If we eliminate u between the expressions for λ and ν, remembering that m is a function of u, we find $V^2 = c^2 + \dfrac{\lambda^2 m_0{}^2c^4}{h^2}$. Thus the waves show dispersion (as they must since the wave and group speeds are different), and in the sense of normal optical dispersion or of that of gravity water waves. The waves go through the group

which constitutes the electron, from behind with great speed; but at present the picture is incomplete because though we have calculated a group velocity, our wave expression is still that of an endless monochromatic wave which, at least when a is constant, has no variation in amplitude and does not constitute a group. The result must be regarded as tentative and requires to be generalized. This is done by invoking de Broglie's second main idea, which is that the waves act as a guide for the particles and determine their motion. The ordinary Newtonian mechanics, or rather their relativistic generalization, are thus to be replaced by laws which involve the conception of waves.

We have seen that wave motion degenerates into ray motion when $v = V$. In such a case Huygens' construction holds in the simple form and from it can be deduced Fermat's principle that $\delta \int_A^B \frac{ds}{V} = 0$. It was pointed out by Hamilton that this principle has a close mechanical analogue, for the Newtonian mechanics of a single particle in a conservative field of force can be summed up in the condition $\delta \int_A^B mu ds = 0$. The integral is called the "action" and is denoted by S. If we take for V the expression found above, namely c^2/u, Fermat's principle becomes $\delta \int_A^B \frac{u}{c^2} ds = 0$, writing $E = mc^2$ this gives $\delta \int_A^B \frac{mu}{E} ds = 0$; for a particle moving in a conservative field E is constant and the above is equivalent to the action equation. Thus in the special cases in which waves of the type considered above are equivalent to rays, these rays are the possible Newtonian trajectories of the particle for different initial conditions. We may, therefore, hope that in the generalized case, in which a translation into geometrical optics is no longer possible, the waves we have considered will con-

tinue to tell us something about the motion of the particles.

We wish to obtain a wave equation of the form

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\nabla^2\psi=\frac{1}{V^2}\frac{\partial^2\psi}{\partial t^2} \qquad (1)$$

If ψ is to vary with the time as $e^{i2\pi\nu t}$ we have $\nabla^2\psi=-\frac{4\pi^2\nu^2}{V^2}\psi$. Now $V = c^2/u = mc^2/mu = h\nu/mu$. On the relativity mechanics $E=\frac{m_0c^2}{(1-u^2/c^2)^{\frac{1}{2}}}+F$, where F is the potential energy, while $mu=\frac{m_0u}{(1-u^2/c^2)^{\frac{1}{2}}}$. Solving for u in the first equation and substituting, we get

$$mu=\frac{1}{c}[(E-F)^2-m_0{}^2c^4]^{\frac{1}{2}} \qquad (2)$$

In ordinary mechanics we have $E' = F + \frac{1}{2}mu^2$ giving

$$mu=[2m_0(E'-F)]^{\frac{1}{2}} \qquad (3)$$

The equations thus become:

$$\nabla^2\psi+\frac{4\pi^2}{h^2c^2}[(E-F)^2+m_0{}^2c^4]\psi=0 \qquad (4)$$

for relativity, and

$$\nabla^2\psi+\frac{8\pi^2m_0}{h^2}(E'-F)\psi=0 \qquad (5)$$

for ordinary mechanics. It should be noticed that the value which this last equation gives for the wave velocity if $F = 0$, is $h\nu/mu = \frac{1}{2}mu^2/mu = \frac{1}{2}u$. The omission of the "energy of constitution" m_0c^2 has entirely altered the wave speed, but the wave-length is still h/mu where we no longer distinguish between m and m_0.

One reason for choosing $h\nu/mu$ as the expression for V, instead of, for example, c^2/u, is that it corresponds to a relativistic generalization of the original equation $E = h\nu$. It is well known that associated with an energy in relativity is a momentum, the whole forming a "four-

vector", while associated with a frequency are three space components; we can take these as proportional to the component wave numbers along the axes. We have, in fact, as one four-vector $(E/c, mu)$ and as another $(\nu/c, 1/l)$ where l is some length. If this is taken as a wave-length there will be a corresponding wave velocity V′ such that $\nu/V' = 1/l$. Now the time component of the first of these four-vectors is h times that of the second. It is reasonable to suppose that the same relation holds between the space components. This means $mu = h\nu/V'$ which, if $V' = V$, is the relation we have used.

The phase of the plane monochromatic wave is $2\pi\nu(t - x/V) = 2\pi/h \cdot (Et - xmu)$. In all cases the variation in phase is $2\pi/h \cdot (E\delta t - mu\delta x)$. The second term is the element δS of the action integral and the whole parenthesis is the change in $Et - S$ which is the so-called Lagrangian action with the sign changed. The phase velocity $v = \dfrac{n}{|\text{grad}\,\phi|} = \dfrac{E}{\left[\left(\dfrac{\partial S}{\partial x}\right)^2 + \left(\dfrac{\partial S}{\partial y}\right)^2 + \left(\dfrac{\partial S}{\partial z}\right)^2\right]^{\frac{1}{2}}}$. For the particular case where Huygens' principle applies in its simple form $v = V = h\nu/p = E/p$, where p, the momentum, is $1/c[(E-F)^2 - m_0^2c^4]^{\frac{1}{2}}$ in the relativity case and $\sqrt{2m_0(E'-F)}$ in the ordinary case. The latter leads to $\left(\dfrac{\partial S}{\partial x}\right)^2 + \left(\dfrac{\partial S}{\partial y}\right)^2 + \left(\dfrac{\partial S}{\partial z}\right)^2 = 2m_0(E'-F)$, the usual form of the Hamilton-Jacobi equation. This shows directly that the use of Newtonian mechanics is equivalent to treating the wave problem by the simplified Huygens method. There is a similar equation in the relativity case.

The wave equation we have obtained is sufficiently generalized to cover any case of the motion of a particle of known energy in a field of force determined by a scalar potential. It does not, as yet, include the effects of magnetic fields. But we have still to consider in what way the motion of the particle is connected with the wave in those cases where the waves are not such as to be equivalent to geometrical optics, and these are of course precisely the

cases in which we are interested, for it is here that we may hope for new results not predicted by the older dynamics. It may be noticed at the start that since $\lambda = h/mu$ the wave mechanics will give results indistinguishable from Newtonian mechanics as h/mu becomes indefinitely small, *i.e.* for heavy bodies and large speeds, for it is well known that wave optics approaches geometrical optics as a limit as the wave-length becomes indefinitely small. De Broglie assumed that the electron is a point singularity in the wave.[1] Such a wave is not a solution of the equation as it stands, but he has shown that the equation can be modified so as no longer to contain the energy explicitly and so that an expression of the form

$$\psi = \frac{c}{\sqrt{x^2+y^2+\frac{(z-ut)^2}{1-u^2/c^2}}} \cos 2\pi\nu(t-uz/c^2)$$

is a solution. This expression represents a wave whose amplitude is proportional to $1/r$, where r is the distance from a center moving with the speed u as measured by an observer going at that speed. The behavior of such a wave when undergoing diffraction or refraction would appear to involve very difficult calculations. It seems, however, almost certain that the reflection of such a wave by a surface of discontinuity would result in two waves each with a singularity. Now electrons can show an effect which is almost certainly equivalent to specular reflection, but there is, of course, no increase in the numbers of the electrons such as one would expect if the number of singularities were to increase, and for these reasons I am inclined to reject the idea of an electron with a point singularity. The other interpretation is that made by Schrödinger who has used Equation (5) with great success in the investigation of the stationary state of atoms. He takes $|\psi|^2$ as a measure of the "electric density." For a single electron this is nearly equivalent to saying that the same quantity measures the probability per unit volume of the presence of the electron at any point. Schrödinger also has modified the equation, so as to eliminate the

[1] L. de Broglie, *J. phys.*, **7**, 321 (1926).

energy, and obtains a form which should hold for all particles of the given mass in the given potential field. In the equation $\nabla^2\psi + \frac{8\pi m_0}{h^2}(E'-F)\psi = 0$, ψ varies with the time according to the factor $e^{i\frac{2\pi}{h}E't}$, thus $E'\psi = \frac{h}{2\pi i}\frac{\partial\psi}{\partial t}$ and making this substitution we have

$$\nabla^2\psi - \frac{8\pi m_0}{h^2}F\psi = \frac{i4\pi m}{h}\frac{\partial\psi}{\partial t} \qquad (6)$$

As long as ψ varies as $e^{i\frac{2\pi}{h}E't}$ this is mathematically identical with the last equation, but it is a more convenient form because it is a single equation which holds whatever the energy of the particle may be, while the former is a family of equations each valid for one particle frequency (or energy). The latter equation has also been assumed to hold in cases when F includes the time explicitly, for example when an electron in an atom is disturbed by the field of an electromagnetic wave. It would be unreasonable to make such a generalization in the former equation, for in a case like this the energy of the electron is not constant.

It has been pointed out by de Broglie[1] and others, that one can arrive at the above equations by a formal process which gives an easy generalization to the case of problems involving more than one particle. Write the equation of energy in the form $E = H(x,y,z;p_x,p_y,p_z)$ where H is expressed as a function of the co-ordinates (which, however, must be rectangular) and their conjugate momenta p_x, p_y, p_z, and E is the numerical value of the energy. Form an operator by replacing p_x by $\frac{h}{2\pi i}\frac{\partial}{\partial x}$, and so on, then the equation in the form containing E is given by $H(x,y,z;\frac{h}{2\pi i}\frac{\partial}{\partial x}, \text{etc.})\psi = E\psi$, and that in the general form by writing

$$H(x,y,z;\frac{h}{2\pi i}\frac{\partial}{\partial x}\ldots)\psi = \pm\frac{h}{2\pi i}\frac{\partial\psi}{\partial t}, \qquad (7)$$

[1] De Broglie, *op. cit.*, p. 31.

where either sign may be taken. Since the function H is the well-known Hamiltonian expression for the energy, this can be generalized directly to any number of particles. For two electrons, for example, the change consists in replacing $\nabla^2\psi$ by $\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)\psi$ where (x_1,y_1,z_1) and (x_2,y_2,z_2) are the co-ordinates of the two electrons. The solution for ψ is thus a function of six co-ordinates and the "waves" cannot be described in three-dimensional space. The solution cannot even, in general, be expressed as the product of a function of (x_1,y_1,z_1) alone into one of (x_2,y_2,z_2) alone.

The presence of "i" in the general wave equation raises some curious points. We are not concerned here, as in the usual oscillation problem, with the real part of ψ but rather with its modulus. Corresponding to any ψ is a conjugate ψ^* which is a solution of the equation with the other choice of the ambiguous sign, $\psi\psi^*=|\psi|^2$ is the quantity which, following Schrödinger, we shall use as expressing a physical reality. In Chapter VII we shall consider the occurrence of imaginaries.

Now that we have an equation which is not limited to monochromatic waves, we can envisage the electron as a group formed of waves of nearly but not quite the same frequency. If the frequency range continuously over a small finite range, such a group will have a prolonged, but finite, region of large amplitude and on each side will tail away to zero. Owing to the great difference in wave and group velocities fresh waves are always entering the group from behind, and disappearing at its front edge. As the group advances it grows longer, for the different elementary groups composing it spread out owing to their difference in speed. The group is not strictly monochromatic and the wave-length varies slightly from point to point, but as the group spreads the variation grows less and less. The speed with which that part of the group advances, whose wave-length differs from λ by less than some assigned small quantity, is u where $\lambda = h/mu$. If λ refers to the main central portion of the group, u is the speed of the particle to which the group most nearly corresponds.

Refractive Index

The wave velocity is $V = c^2/u$. If the particle is accelerated V changes and the corresponding waves will change from a nearly monochromatic wave corresponding to one value of V to one corresponding to another. Now $V = c^2/u = c^2(m/2T)^{\frac{1}{2}}$ where T is the kinetic energy and relativity is neglected. For a conservative field of force $T = E' - F$ and $V = c^2[m/2(E'-F)]^{\frac{1}{2}}$. This gives a second type of dispersion, one which depends on F. We may express the result by saying that a field of force of potential energy F has a refractive index for a particle of energy E′ given by $\mu = (1 - F/E')^{\frac{1}{2}}$. The same result can be obtained from Equation (5) by comparing it with $\nabla^2\psi = \frac{1}{V^2}\frac{\partial^2\psi}{\partial t^2}$.

THEORY OF QUANTA IN RADIATION

The theory we have been considering in this chapter was originally invented largely to explain the peculiar behavior of radiation, as shown in Planck's law and in the contrasting effects of interference and the photo-electric effect. Following an idea of Einstein's, de Broglie supposed that radiation contained particles or "quanta" of energy $h\nu$. The new theory was an attempt to account for interference and diffraction by supposing that the waves controlled the motion of these particles, and that they became most densely distributed where the intensity of the light wave was greatest. In this form the theory closely resembles one put forward some years ago by Sir J. J. Thomson,[1] which regarded the wave front of light as "spotted", each spot corresponding to the intersection of the wave front with one of a number of discrete tubes of force, along which alone the energy was propagated. To fit the observed facts it is necessary to suppose that the "particle" or quantum of light has a velocity u indistinguishable from c, the velocity of light in the theory of relativity. The virtual mass $m = \frac{m_0}{(1-u^2/c^2)^{\frac{1}{2}}}$ will thus be very large compared with m_0. De Broglie at first supposed that u was less than c by a finite amount, and that the

[1] J. J. Thomson, *Electricity and Matter* (New York, 1904), page 63.

resting mass m_0 of the light quantum was small but finite, being chosen to make the energy $mc^2 = \frac{m_0c^2}{(1-u^2/c^2)^{\frac{1}{2}}} = h\nu$. It was pointed out, however, that this leads to difficulties. The theory leads to the expression $V^2 = c^2 + \frac{\lambda^2 m_0{}^2 c^4}{h^2}$, V is thus greater than c, and though the difference vanishes with m_0, for any finite value of m_0 we have only to make λ large enough to make the difference easily perceptible. Now it is precisely for the very long electromagnetic waves that the agreement between experiment and the classical theory is most complete, and no such change of velocity in fact occurs.

It is possible to avoid the difficulty by making m_0, a true infinitesimal, and u differ only infinitesimally from c in such a way that the above energy equation continues to hold. This seems, however, rather artificial and one is inclined to think that the duality between waves and particles is a more fundamental fact in the world than de Broglie's mathematical theory, which may only be a suitable expression of it in the case of material particles. Be this as it may, there is no doubt that the successes of the theory as applied to electrons have greatly strengthened the belief that the explanation of the difficulties in optics to which reference has been made, is to be found in regarding light as consisting of particles guided by waves.

STATIONARY STATES

Although it is not proposed in this book to deal with that part of wave mechanics which refers to the behavior of the electrons forming part of an atom, yet it seems desirable to describe briefly the original application of waves to this problem, even though later developments have shown it to be approximate only. The Bohr theory of the atom was based on the conception of favored orbits which alone were permanent. These were the orbits for which the moment of momentum of the electron was a multiple of $h/2\pi$. This result was extended by Sommerfeld to the form $\oint pdq = nh$ where p is the momentum conjugate to the periodic co-ordinate q and the integral is taken over

a period. These conditions were quite arbitrary, and justified only by their success in explaining spectra.

On de Broglie's theory the space round a nucleus has a refractive index for electron waves which varies with the distance from the nucleus, the waves far out travelling faster. The result is that an electron wave once started could travel round the nucleus with its wave front radial, by a process somewhat similar to that by which the light waves are bent in a mirage, and the sound waves of an

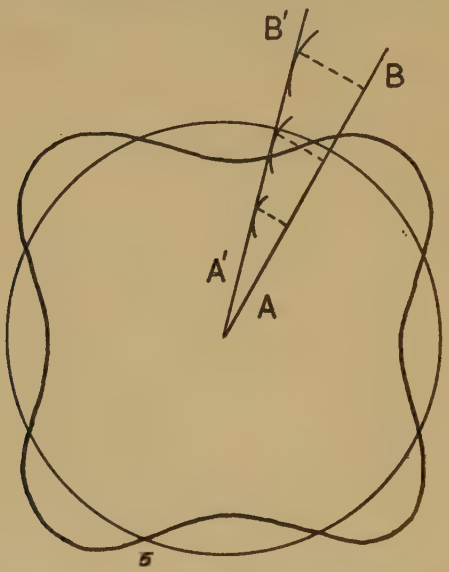


FIG. 5

explosion are believed to be bent round the earth by refraction in heated upper layers of the atmosphere. Thus, in Figure 5 the wave front $A'\ B'$ is generated from $A\ B$ by Huygens' construction.

When the waves return to their starting point after passing once round the nucleus they will not, in general, be in phase with the waves there, but for certain particular lengths of path they will be so, namely for those which are an exact multiple of the wave-length. It is rather like papering a room with a patterned wall paper; only for certain sizes of room will the pattern fit exactly at the joint. For a circular path (see Fig. 5) and therefore constant

speed of the electron λ is constant $= h/mu$, therefore $2\pi r = nh/mu$ and $mur = nh/2\pi$, n being an integer, which is Bohr's condition. In the more general case $\phi = 2\pi(Et - S)/h$, if this changes by $2\pi n$ round a cycle at a given time, S, the "action" taken round a cycle, is a multiple of h, which is an extended form of the condition. The Sommerfeld conditions were also explained by de Broglie by an ingenious extension of this argument. Though this gives a very graphic explanation of Bohr's conditions the exactness of the agreement is partly fortuitous. The waves cannot be regarded as confined to a narrow track, like the old conception of an electronic orbit. Their wave-length being comparable with the size of the orbit, they must fill the space round it. The wave-length, at the orbit which the particle is supposed to travel, fits the condition; and so it does to a first order at places near, if the wave-length is assumed to change according to the refractive index we have given, but the result is not general throughout the volume of the atom. It is not justifiable to treat the motion of waves, in a region comparable with their wave-length, by methods which are really equivalent to Huygens' principle rather than to a proper use of the wave equation. Nevertheless, the method helps one to see the physical meaning of the exact mathematical processes used by Schrödinger in the application of Equation (5) to the hydrogen atom. These are outside the scope of this book.

CHAPTER III

Theory of Wave Diffraction by Crystals

As most of the experiments with which we shall be concerned in the following chapters deal with the diffraction of electron waves by crystals, it seems desirable to include here some account of the theory of crystal diffraction as worked out for X-rays. No attempt will be made to deal fully with this subject, which already has a very large literature, we shall consider only those results which are required for our immediate purpose.

A crystal may be defined as a solid whose structure repeats itself periodically in each of three dimensions. The smallest element from which the whole structure can be built by a mere process of repetition is called the "unit cell". This "unit cell" can always be taken as a parallelopiped. If a number of these parallelopipeds are placed together as in the crystal, their corners form a three-dimensional array of points called the "crystal lattice". The lattice of points can be supposed moved parallel to itself in any way, it being immaterial what point of the repeating pattern is taken as representative of the unit. The cell corresponding to a given point lattice can be drawn in an infinite number of ways. The dotted lines in Figure 6 show one way, other ways are indicated by the full lines. The unit cell has, necessarily, always the same volume, being the smallest volume from which the crystal can be built by repetition.

Directions parallel to a set of three intersecting edges are called the directions of the crystal axes, and the lengths of these edges are the lengths of the axes. Any possible natural surface of the crystal passes through a set of lattice points called a "net plane", though many such net planes seldom or never occur as natural surfaces. If the lengths of the axes are a, b, c, then the equation of a net

plane through points on the axes at p, q and r units from some lattice point taken as origin is:

$$\frac{x}{pa}+\frac{y}{qb}+\frac{z}{rc}=1 \qquad (1)$$

The axes are, of course, in general oblique. If $x'=x/a$, $y'=y/b$, $z'=z/c$, the equation of the plane may be written $qrx'+rpy'+pqz'=pqr$. This may be reduced to

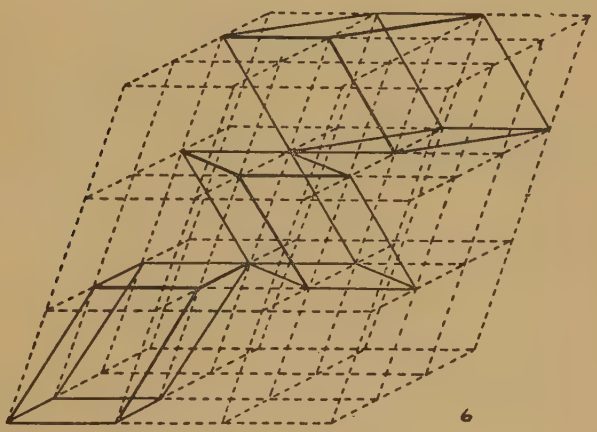


FIG. 6

$hx'+jy'+kz'=$ *an integer*, where h, j, k, have no common factor. The integers (hjk) are known as the Miller indices of the set of planes parallel to the above. One of these planes is:

$$hx'+jy'+kz'=1 \qquad (2)$$

It is a known algebraical theorem that this equation has an infinite number of solutions in integers for all integral values of (hjk) prime to each other, negative integers being admitted. The set of planes:

$$hx'+jy'+kz'=N \qquad (3)$$

clearly has also an infinite number of integral solutions in x',y',z', for all integral (and zero) N, and planes for successive values of N are equally spaced. Now a point characterized by integral values of x', y', z', is a lattice

point, so that we have a set of equally spaced planes each passing through a (doubly) infinite set of lattice points, the one through the origin being

$$hx' + jy' + kz' = 0 \qquad (4)$$

and the next $hx' + jy' + kz' = 1$ or $hx/a + jy/b + kz/c = 1$. Clearly if N is not an integer, no integral values of x', y', z', can satisfy the equation. Equation (3) represents the complete set of planes in this direction.

DIFFRACTION

Each unit cell of the crystal lattice contains the same amount of matter similarly arranged. Suppose that plane waves fall on the crystal and that, to take the simplest

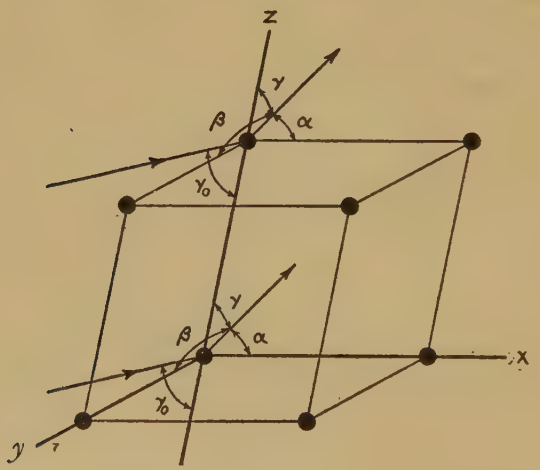


FIG. 7

case first, each unit cell contains one particle capable of scattering the waves. We wish to determine in what directions, if any, the scattered waves will reinforce one another. We may draw the crystal lattice so that the lattice points fall on any part of the pattern of which the crystal is formed. Choose the scattering points as in Figure 7. Then if the incident wave normal makes angles, α_0, β_0, γ_0, with the axes, and we consider parallel scattered rays in a direction with angles α, β, γ, the path difference between

the rays from the scattering point at the origin and that from the point at $(a00)$ is $a(\cos\alpha_0 - \cos\alpha)$. Similarly the path differences for the rays from $(0b0)$ and $(00c)$ are $b(\cos\beta_0 - \cos\beta)$ and $c(\cos\gamma_0 - \cos\gamma)$, respectively. The scattered rays are taken as parallel, because we shall be observing effects at a distance from the crystal very large compared with the distance apart of the atoms. If, now, we have simultaneously:

$$a(\cos\alpha_0 - \cos\alpha) = l\lambda$$
$$b(\cos\beta_0 - \cos\beta) = m\lambda$$
$$c(\cos\gamma_0 - \cos\gamma) = n\lambda$$

where l, m, n, are integers, and λ is the wave-length of the rays, then the diffracted rays, not merely from the four lattice points which we have considered but from all points of the crystal lattice, will be in phase. For we can proceed from the origin to any point of the lattice by a repetition of steps corresponding to the three axes, and each of these steps is shown by the above equations to involve a path difference of a whole number of wave-lengths. If λ is given and α_0, β_0, γ_0, there are three equations for α,β,γ; but these last are not independent, being connected with the angles between the axes by an identical relation, *e.g.* if the axes are rectangular.[7]

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1.$$

Thus, in general there is no solution of the above equations and no diffracted beam with monochromatic waves. If, however, white light is used a number of solutions become possible corresponding to different choices of the integers (lmn). These in the case of X-rays form the well-known Laue patterns obtained when "white" X-rays are passed through a single crystal and received on a photographic plate.

The conditions for a diffracted beam have been expressed in a different and very convenient manner by W. L. Bragg. The waves from a lattice point at $(x'y'z')$ will agree with those from the origin in a direction α,β,γ, if, on the above notation,

$$x'a(\cos\alpha_0 - \cos\alpha) + y'b(\cos\beta_0 - \cos\beta) + z'c(\cos\gamma_0 - \cos\gamma) = \lambda(lx' + my' + nz') = 0 \quad (5)$$

this represents a plane through an infinite number of lattice points.

Now the condition that the scattered rays, in a certain direction from a number of points in a plane illuminated by parallel light, shall be in phase (path difference *zero*) is that the direction shall be that of the reflected ray as given by geometrical optics. This is easily seen from the fact that the Huygens construction gives the law of reflection by a plane.

Conversely, if we take a direction corresponding to reflection from one of the planes of the crystal, all the scattering centers in that plane will be in phase. The same will be true of any parallel plane, and the condition that

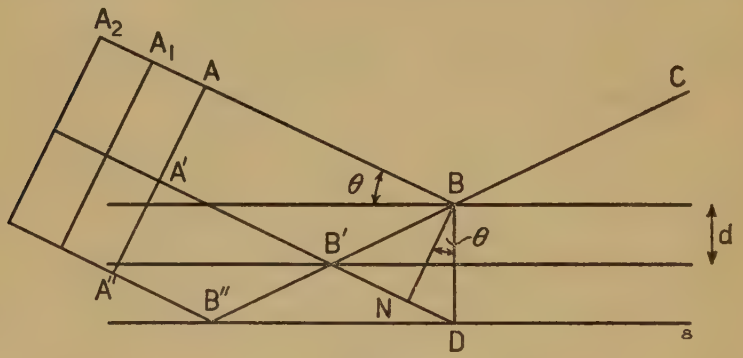


FIG. 8

the whole reinforce reduces to the condition that reflected waves from a series of parallel planes shall strengthen each other. This condition can easily be found. In Figure 8 let BC be the reflected ray and AB, $A'B'$, be incident rays. Let $AA'A''$ be perpendicular to AB. The condition is that $AB + BC + N\lambda = A'B' + B'C$ or $N\lambda = B'B + A'B' - AB$. Produce $A'B'$ to cut the third plane in D and draw BN perpendicular to $A'D$. Then $B'D = B'B$ and $B'B + A'B' - AB = ND = 2d\sin\theta$ where θ is the glancing angle. Thus the condition is $2d\sin\theta = N\lambda$. This gives the angle at which a crystal plane must be set to give an intense diffracted beam by "reflection."

By comparing Equations (4) and (5) we see that the Miller indices (hjk) of a Bragg plane are proportional to the Laue numbers (lmn) corresponding to the same spot. If (lmn) have a common factor N′ this will be the least

number, other than *zero*, to which the expression $lx' + my' + nz'$ can be equal for integral values of x', y', z'. It is, therefore, the number of wave-lengths path difference between the atoms in one Bragg plane and those in the one which lies nearest it. Thus N′ is equal to the Bragg N, the "order" of the reflection.

To apply the Bragg law we need to know the distance between successive planes. If λ,μ,ν, are the angles *yoz*, *zox*, *xoy* between the axes, the length of the perpendicular from the origin on the plane $hx/a + jy/b + kz/c = 1$ is d, where:

$$d^2 = \frac{1 - \cos^2\lambda - \cos^2\mu - \cos^2\nu + 2\cos\lambda\cos\mu\cos\nu}{\frac{h^2}{a^2}\sin^2\lambda + \frac{j^2}{b^2}\sin^2\mu + \frac{k^2}{c^2}\sin^2\nu + 2\frac{bj}{ab}(\cos\mu\cos\lambda - \cos\nu) + \frac{2jk}{bc}(\cos\mu\cos\nu - \cos\lambda) + \frac{2kb}{ca}(\cos\lambda\cos\nu - \cos\mu)}$$

Bragg's law runs:

$$\sin\theta\Lambda = \left[\frac{\frac{l^2}{a^2}\sin^2\lambda + \frac{m^2}{b^2}\sin^2\mu + \frac{n^2}{c^2}\sin^2\nu + \frac{2mn}{bc}(\cos\nu\cos\mu - \cos\lambda) + \frac{2ln}{ca}(\cos\lambda\cos\nu - \cos\mu) + \frac{2lm}{ab}(\cos\mu\cos\lambda - \cos\nu)}{1 - \cos^2\lambda - \cos^2\mu - \cos^2\nu + 2\cos\lambda\cos\mu\cos\nu}\right]^{\frac{1}{2}}$$

where Λ is written for the wave-length to avoid confusion with the angle, and the "order" N is allowed for by writing (l,m,n) for $N(h,j,k)$. For rectangular axes this reduces to

$$2\sin\theta = \sqrt{l^2/a^2 + m^2/b^2 + n^2/c^2}$$

and for cubic axes,

$$2a\sin\theta = \lambda\sqrt{l^2 + m^2 + n^2}$$

where a is the side of the unit cube.

STRUCTURE FACTOR

So far we have considered only one scattering point in each unit cell. If there are many, or if there is a continuous distribution of scattering matter, the above analysis gives the condition that the wave scattered by any one point shall reinforce that from the corresponding point in the other unit cells. The scattered waves from the different points in each unit cell will interfere among themselves, reinforcing in some directions and tending to cancel in others. The resultant intensity will thus be the product

of two factors, one of which has maxima, as found above, in directions determined by the crystal axes and the indices (l,m,n). The other depends on the grouping of the scattering matter in the unit cell. The second factor may cause the entire disappearance of some of the maxima and the weakening of others; but of course it can never cause a diffraction maximum in a place not given by the above formula.

CUBIC CRYSTALS

While there are comparatively few crystals whose unit cell is a cube, there are a large number which can be represented by equal rectangular axes, by a slight artifice. These are the crystals which belong to the body-centered and the face-centered cubic types. The lattices of these crystals

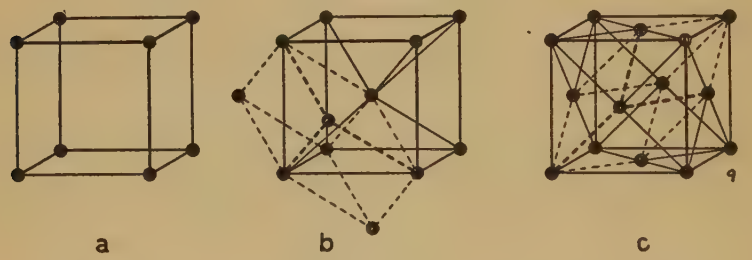


FIG. 9

are shown in Figure 9(b) and (c), together with the simple cubic lattice at (a). Take Figure 9(b): if we place at the center of a simple cube, a point representing exactly the same atom or group of atoms as that represented by the points at the corners, we obtain a "body-centered cube". A lattice made up of these has twice as many points as a simple cubic lattice of the same size.[1] The cube is no longer the unit cell for it contains two units. One way in which a true unit cell can be drawn is shown by the dotted lines (Fig. 9) but it is far more convenient to keep to the rectangular axes, though it means taking into account the interference between the waves scattered by the two units in the cube. For example, take a plane perpendicular to one of the cubic axes. The spacing is no

[1] Note that a point at the corner of a cube is shared by 8 cubes and counts 1/8, similarly a point on an edge counts 1/4 and one on a face counts 1/2.

longer equal to the cube edge, but is halved, for other parallel planes can be drawn through the centers of the spheres; these contain the same density of points as the original ones. Hence all the odd orders of reflection from this plane will be destroyed by the interference of the waves from the two kinds of planes. In general if l,m,n, are Laue numbers corresponding to a certain direction α,β,γ, the path difference between rays from opposite points of a cube diagonal is $(l+m+n)\lambda$, and that between the origin and the center of the cube is $\frac{1}{2}(l+m+n)\lambda$. Hence for the center points to be in phase with the others $l+m+n$ must be even. The other diffraction maxima will be destroyed by interference.

Figure 9 shows at (c) a face-centered cube formed by adding a group at the center of each cube face. The cube now contains 4 groups, whose co-ordinates may be taken to be (000), $(\frac{1}{2}\frac{1}{2}0)$, $(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}0\frac{1}{2})$. The condition for phase agreement between these and the original point is $\frac{l+m}{2}, \frac{m+n}{2}, \frac{n+l}{2}$, all integers. This implies that l,m,n are all even or all odd. The first few possible sets are thus (111), (200), (220), (311), (222), (400).

"POWDER" METHOD

A method which has been used a great deal in the examination of metals by X-rays is the Hull-Debye-

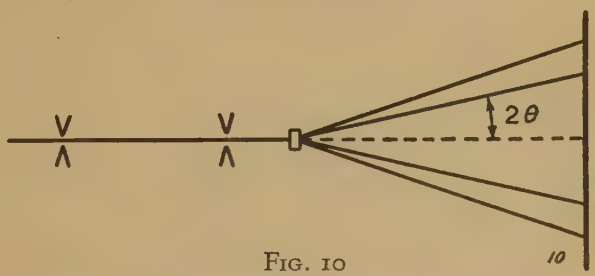


FIG. 10

Scherrer method. If a substance composed of a vast number of very small crystals oriented at random is irradiated by monochromatic X-rays, some among the crystals will be set at such an angle that they are in the right attitude to reflect the X-rays from one particular face. If there

are sufficient crystals reflections will be found from every possible face. The deviation of the rays from the direction of the original beam is 2θ where $2d\sin\theta = N\lambda$ (Fig. 10). The diffracted rays thus form a series of cones round the incident beam as axis, one for each value of d. If a photographic plate is placed perpendicularly to the incident beam, the intersections of these cones will give a pattern of concentric circles on the plate. Each point on one of the circles is caused by a different fragment of crystal, and if the crystals are not sufficiently numerous or are not arranged entirely at random with regard to the direction of the incident rays, the circles may be incomplete and appear as a series of spots or as arcs varying in intensity. As in the case of the optical diffraction grating, high resolving power requires the co-operation of a large number of diffracting centers and if the crystals are too small the rings will be broadened. Since the crystals are arranged at random, waves from one crystal will have no definite phase relation with those from another, and there will be no interference between them.

ELASTIC COLLISIONS

It should be noticed that for constructive interference to occur between the scattered waves they must all have the same period, in practice that of the initial waves. For electron waves the period is determined by the energy of the electron, thus scattering can only lead to regular diffraction patterns if it takes place without loss of energy or, in the language of particles, if the collision is elastic. Collisions which involve loss of energy undoubtedly occur between electrons and atoms, but electrons scattered in these collisions would not show diffraction effects in their distribution, unless indeed there was a finite probability of a number of electrons having exactly the same energy loss. If this occurred, and there was agreement in the phase with which the scattered wavelets started, one would get a pattern corresponding to the new wave-length.

CHAPTER IV

The Experimental Evidence

It was suggested by Elsasser[1] that evidence for the wave nature of electrons would be found from their interaction with crystals. Clearly, very strong support for the theory would be obtained if it were possible to measure some quantity which could be regarded as a wave-length, and if it were found that the values agreed with the formula $\lambda = h/mu$. The measurement of a wave-length suggests a diffraction grating, which is in essence a device for producing a number of regularly spaced wavelets from one primary wave. If we substitute the numerical values of h and m in the above formula and write $\frac{1}{2}mu^2 = eP/300$, where P is the potential drop in volts equivalent to the energy of the electron, we get:

$$\lambda = \sqrt{\frac{150}{P}} \times 10^{-8} cm \qquad (1)$$

Thus for electrons of manageable hardness the wave-lengths are comparable with those of X-rays. For the measurement of X-ray wave-lengths crystals are used, each atom of which may be regarded as producing a scattered wavelet, the wavelets from corresponding atoms in the different unit cells having phases whose regular relations we have considered in Chapter III. Now electrons also are scattered by atoms, in some cases without loss of energy or change of wave-length, and it was thus reasonable to hope that the interference of these wavelets should give similar effects to those obtained from X-rays.

Davisson's and Germer's experiments

The first experiments on these lines were made by Davisson and Germer.[2] The general idea was that a beam of homogeneous electrons, of energy varying in different

[1] W. Elsasser, *Naturwissenschaften*, 13, 711 (1925).
[2] C. Davisson and L. H. Germer, *Phys. Rev.*, 30, 707 (1927).

experiments from 65 to 600 volts, was allowed to fall normally on a single crystal of nickel cut with a (111) plane in the surface. Nickel forms face-centered cubes. The scattered electrons were received in a Faraday cylinder which could be moved so as to receive electrons coming from the crystal at any required angle to the normal, within limits. A back potential of 9/10 of the original

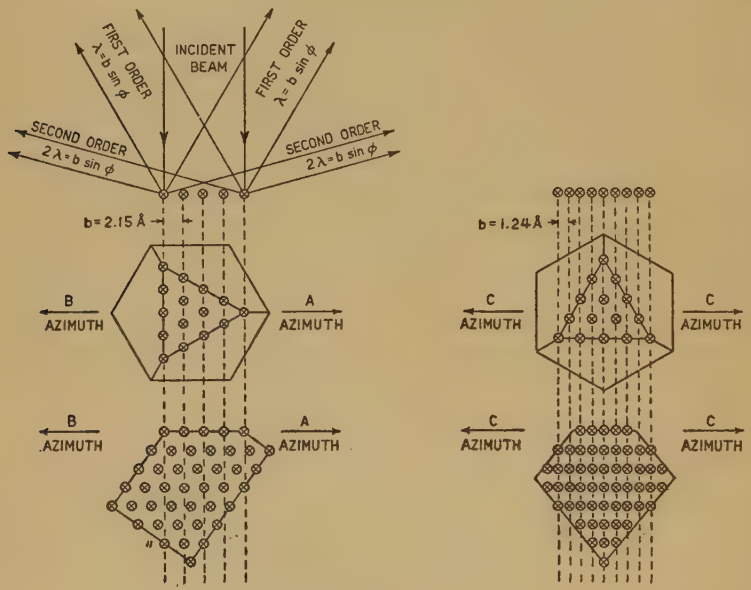


FIG. 11

potential of the electrons was applied between the cylinder and the crystal, so that electrons which had lost more than 10 per cent of their energy were excluded. The crystal could be rotated about the normal to the face used, relative to the plane containing this normal and the Faraday cylinder. In the 360° of motion in azimuth thus obtained certain positions correspond to specially asymmetrical relations of the crystal atoms to the plane containing the cylinder and normal. These positions are indicated in Figure 11. The *C* azimuth occurs six times in a revolution, *A* and *B* three times each. The difference between the *A* and *B* azimuths only comes in for the atoms below the

surface. The surface layer is identical as viewed from either direction, but the layer below is staggered by 1/3 of the spacing of the top layer and thus is placed differently with respect to the latter in the two aspects (See Fig. 12).

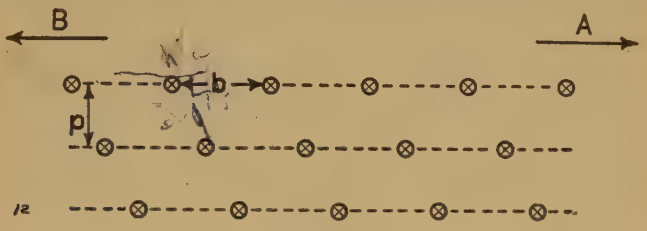


FIG. 12

If observations are made in one of these azimuths using electrons of arbitrary voltage and changing the position (co-latitude) of the collector a curve like that to the left in Fig. 13 will, in general, be obtained. The radius vector indicates the intensity of scattering in a given direction. This curve

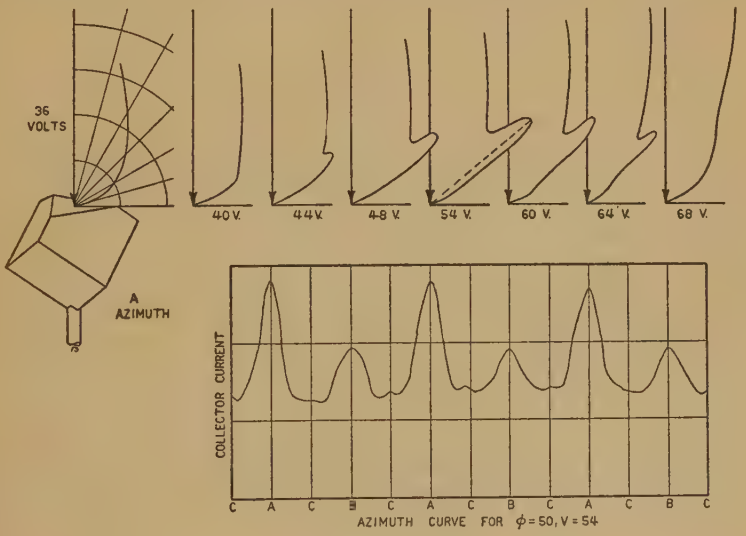


FIG. 13

shows a steady increase of scattering towards the normal. If, however, a series of such curves are obtained with varying electron speed, it is found that a pronounced spur develops

(Figure 13, to the right). This spur is most marked at a certain voltage, but is visible over a considerable range. The angle of co-latitude of the spur changes at the same time. If the crystal is then rotated in azimuth, with the co-latitude of the Faraday cylinder and the voltage of the rays kept constant, a series of changes occurs as shown in the lower part of Figure 13. The spur—in this case originally in azimuth *A*—repeats thrice in a revolution, as it must from the crystal symmetry; it also occurs in a reduced form in the associated azimuth *B*, again three times.

An exactly similar result occurs if the original observations are made in the *B* azimuth. Again a spur is found, this time it is best developed at 50 volts energy and 44° co-latitude, but now the spur repeats itself in each *B* azimuth and with diminished intensity in the three *A* azimuths. These minor maxima correspond to the spur we first considered, but the voltage and angle are not such as to bring it to its full development. Similar effects occur in the *C* azimuth but here the effect repeats six times in a revolution. In the original experiments 24 of these spurs were found: 9 in the *A* azimuth, 10 in the *B*, and 5 in the *C* azimuth. The natural interpretation is to regard each of these as analogous to an X-ray diffraction beam reflected from some Bragg plane. For purposes of analysis it is, however, convenient to proceed in a slightly different way. The electrons have very little penetrating power so that only a few layers of the crystal are effective in scattering. The result is a lack of resolving power; it is like using a grating with only half-a-dozen lines. This explains, to some extent, the diffuseness of the spurs and their occurence over a wide range of voltage; for, of course, regarded as Laue beams they should occur only with one definite wave-length. Let us take the extreme case and suppose only the top layer of atoms effective. Then we have a plane grating, and for normal incidence we shall get a diffracted beam wherever

$$n\lambda = b\sin\phi, \qquad (2)$$

where ϕ is the angle which the diffracted beam makes with the normal and b is the grating constant, in this case the distance between successive rows of atoms running

perpendicularly to the azimuth investigated. For the general case this relation will also hold, but there is the extra restriction that the lower layers (separated by the distance p) must also be in phase. For the B azimuth (see Fig. 12), this gives:

$$p \cos \phi + \frac{b}{3} \sin \phi = n'\lambda.$$

Eliminating λ we find $\tan \phi = p/b \frac{n}{n' - n/3}$. For the A azimuth $\tan\phi = p/b \frac{n}{n' + n/3}$, and in the C azimuth we have simply $\tan\phi = pn/b'n'$. Calculation shows that $b = \sqrt{3/8}.a$, $p = a/\sqrt{3}$, $b' = a/\sqrt{8}$, where a is the side of the unit face-centered cube. Thus for the A and B azimuths:

$$\tan\phi = \sqrt{9/8} \frac{n}{n' \pm n/3} \qquad (3)$$

Davisson's method is to plot λ or rather $\sqrt{\frac{150}{P}} \times 10^{-8}$ against $\sin \phi$. For each value of n, *i.e.* each order of reflection from the plane grating, he draws the straight line $b/n.\sin\phi = \lambda$, the observed beams should all lie on one of these straight lines if they obey the plane law, and if they also obey the space law the values of ϕ should be given by Equation (3). Actually Davisson and Germer found the first requirement satisfied, but not the second (Fig. 14). We shall discuss the reason for the failure in the second case in Chapter V; the first result is strong confirmation of de Broglie's theory, for not merely does it give the right variation of $\sin\phi$ with P, namely $\sqrt{P}\sin\phi$ constant,[1] but the value of the constant checks de Broglie's law, $\lambda = h/mu$, absolutely, there being no adjustable constants. Thus for the 54-volt beam illustrated in Figure 14, $b\sin\phi = 1.65 \times 10^{-8}$ while $(150/P)^{\frac{1}{2}} = 1.67$, so that the beam is a first-order one. Similarly for the 65-volt beam $b\sin\phi = 1.50 \times 10^{-8}$ and $(150/P)^{\frac{1}{2}} = 1.52$. In some

[1] That is, the same for all the beams when developed to their maximum. It appears not to be true for the variation with voltage of the position of a single beam.

of the other cases the discrepancy was greater. The figures show the extent of the agreement graphically; the displacements of the points from the (calculated) lines do not exceed the error to be expected, owing to the relatively large size of the collector and the fact that there was a small error in the cutting of the crystal face. If, however, a series of integers is substituted for n' in Equation (3) the resulting values of ϕ do not give the positions of the

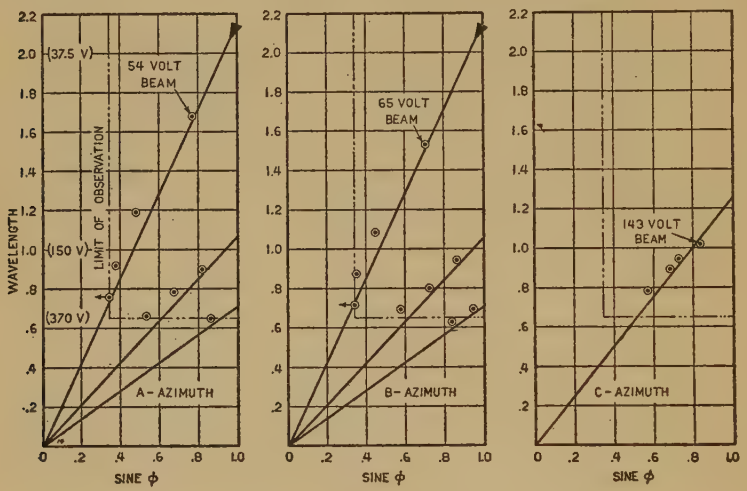


FIG. 14

observed spots, though the number is about the same over the whole range; thus, while the surface layer of atoms scatters according to the simple law, other considerations have to be taken into account to explain the behavior of the lower layers. In addition to the beams here considered, which appear under the best vacuum, Davisson and Germer found others which were apparently associated with the presence of layers of gas on the surface of the crystal. These will be discussed in Chapter X.

In addition, they found in each azimuth a beam near grazing incidence, shown in Figure 14 by the wedge-shaped marks. In the *A* and *B* azimuths it occurred at 32.5 volts and moved up with increasing voltage.[1] This is exactly

[1] It is not apparent on Fig. 14, which refers to experiments taken before the final heating of the crystals, which was needed to bring out the grazing beams.

the voltage to be expected for a plane-grating beam, and the equivalence in the *A* and *B* azimuths also suggests this explanation. The beams increased in intensity at first as the voltage increased, and then decreased again, all the time moving up from the surface. At very small glancing angles the radiation from the lower layers of atoms will not get through, as the angle increases it begins to do so and weakens the surface beam by interference. This explanation does not account for the initial rise in intensity unless this can be attributed to a change in the scattering

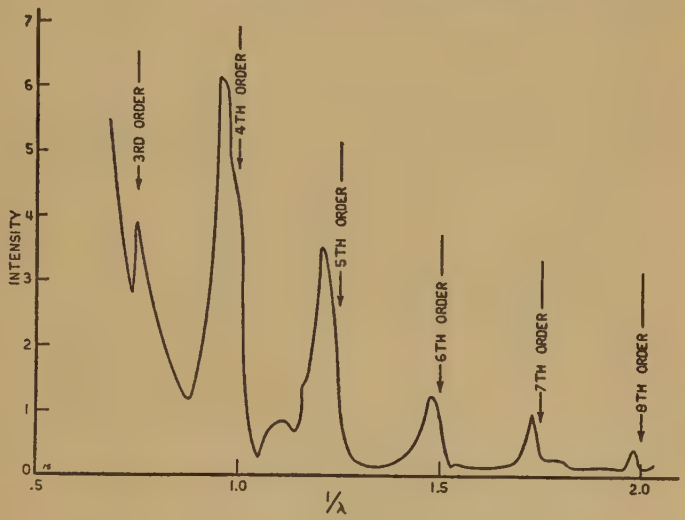


FIG. 15

for a single atom. It is probable that the beam in the *B* azimuth is really a space-grating effect. These beams have not been found with a second apparatus. Three space beams which should, theoretically, have occurred in azimuths other than the principal ones were not observed. Their absence may, perhaps, be explained by the considerations discussed on page 94.

In a more recent paper the same authors have described experiments in which the angle of incidence of the rays was altered. The range used was from 10° to 52° (later 70°). In all cases a beam was found in the direction of specular reflection, and it was this which was chiefly investigated.

As the wave-length is varied the intensity of reflection changes, and if the Bragg law were satisfied we should have $\frac{2}{\sqrt{3}} a \cos\phi = N(150/P)^{\frac{1}{2}}$, since $a/\sqrt{3}$ is the spacing of the (111) surface planes. Figure 15 shows that while the general nature of the effect is as predicted, the exact position of the predicted maxima—shown by the arrows—as a rule does not agree with the most marked maxima on the experimental curve. The possible explanations of this will be discussed in Chapter V.

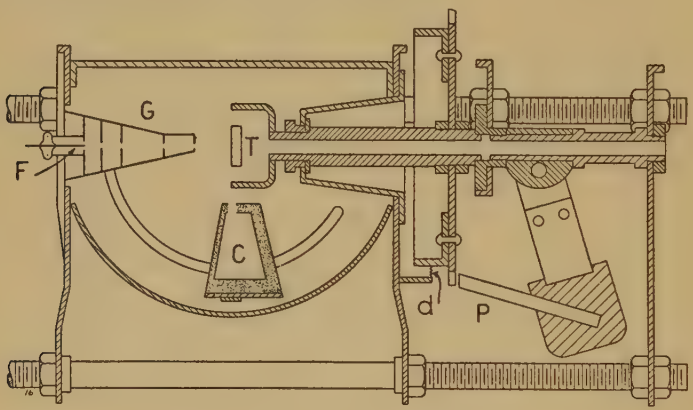


FIG. 16

Experimental Details

A cross section of the apparatus is shown in Figure 16. A tungsten filament, *F*, serves as the source of electrons which are accelerated through the "electron gun" *G*. The outer walls of *G*, the target *T*, the outer box of the collector *C*, and the box enclosing these parts are maintained always at the same potential. Electrons leaving the target with energy less than 90 per cent of that of the initial beam are excluded from the collector by a retarding potential between the inner and outer boxes of the latter. The two parts of the collector are insulated from each other by quartz; the openings in the inner and outer boxes are circular, their diameters being 1.0 mm. and 2.0 mm. respectively. The collector is suspended by arms from bearings outside the enclosing box and is free to rotate

about a horizontal axis normal to the plane of Figure 16, passing through the bombarded area. Its position is adjusted by rotating the whole apparatus, which is sealed from the pump, about this axis. The position can be read from a pointer outside the box (not shown in Fig. 16). The distance from the opening of the gun to the bombarded area is 7 mm. and from this to the opening in the outer box is 11 mm.

The target can be rotated about an axis perpendicular to its face by means of the mechanism shown on the right side of Figure 16. If the tube is rotated counterclockwise about the collector axis, so as to bring the collector into position to catch the electrons, the molybdenum plunger *P*, attached to a heavy pendulum, passes through an opening in a toothed wheel locked to the target and engages with the milled edge of a strip of molybdenum attached to the frame. The target is then locked. If, however, the apparatus is rotated clockwise through a small angle with the horizontal, the plunger disengages from the milled edge *d* but remains in the opening of the toothed wheel. The pendulum, with the engaged wheel and the target are then free to rotate about a fixed hollow shaft normal to the target face. The range of this rotation is only 20° to 30°, but by tilting the apparatus further in a clockwise direction the plunger can be withdrawn from the slot in the toothed wheel, and the pendulum is then disconnected from the target and its shaft. By a rotation about the axis of this shaft, the plunger can be brought back into another slot in the toothed wheel and the rotation of the latter can be repeated. Thus by a step-by-step process any desired rotation can be given to the target.

The target was a block of nickel 8 x 5 x 3 mm. cut from a bar in which crystal growth had been induced by straining and annealing. Crystal facets were developed by etching which, in nickel, usually gives a (111) face. The faces so formed were examined by optical reflection and the crystal was cut approximately parallel to one of them. The surface so exposed was polished, etched, examined and corrected. A photomicrograph was taken of the surface, and the best area selected for bombardment.

A small tungsten filament (not shown) was mounted behind the target and supplied electrons for heating the latter by bombardment.

Great care was taken with the vacuum conditions. The metal parts of the apparatus were preheated to 1000° and were then assembled and sealed into the bulb with the least possible delay. The bulb was of pyrex and had sealed to it two auxiliary tubes, one containing coconut charcoal, and the other a mischmetall vaporizer. During the pumping, which lasted several days, the tube itself and the tubing connecting it with the pumps were baked for hours at a time at 500°. This baking was alternated by the heating by bombardment of such of the metal parts as could be reached from the filaments. The target in particular was heated several times to a temperature at which it vaporized freely. The tube was sealed from the pumps while the target was at a high temperature and the charcoal at 400° to 500° (it had previously had a prolonged heating at 550°). The pressure at the time was 2 or 3×10^{-6} mm. The mischmetall was vaporized when the pumping was nearly completed; it improves the vacuum by forming solid compounds with the residual gas. As soon as the tube with the charcoal had cooled sufficiently it was immersed in liquid air. No means were available for measuring the final pressure, but from previous experience it was estimated at 10^{-8} mm. or less. In making the measurements the current from the filament to an (insulated) diaphragm of the gun was kept constant. The ratio of collector to bombarding current in these experiments was of the order 10^{-4}, the latter being of the order 10^{-6} ampère, and the collector currents were measured with a sensitive galvanometer. The total integrated current of full-speed scattered electrons was 1/10 to 1/20 of the incident beam. The proportion of full-speed electrons in a diffracted beam was much larger than in the diffusely scattered background. The beams appeared to contain, in addition to full-speed electrons, others which had lost energy up to a quarter of the original amount. Owing to the variation with angle, of the background scattering, the beams are, as it were, added on to a sloping curve; the apparent maximum is

therefore probably not the true one. An allowance for this was made by sketching in an assumed background and subtracting from the observed curve to give the part due to the beam itself. The relative intensity of the beams to the background was greatly increased by heating the target shortly before an observation. In these conditions "the ratio of full-speed electrons scattered into any one of the most intense sets of beams to the total number scattered in all directions is about two-tenths".[1]

TRANSMISSION EXPERIMENTS

The first experiments to indicate a diffraction of electrons by thin films were carried out at my suggestion by the late Mr. A. Reid at Aberdeen. The apparatus was an adaptation of one which had previously been used for measuring the scattering of positive rays in gases. A beam of cathode rays from a gas discharge tube was passed through a fine tube and then deflected by an electrostatic field. The deflected beam passed through a hole 0.25 mm. in diameter in a diaphragm, immediately behind which was mounted a thin film of celluloid. After passing through the film the rays travelled a distance of 20 cm. and then struck a photographic plate so placed as to be normal to the beam. The patterns formed by the impact of the rays on the plate consisted of an intense central spot due to the unscattered rays, surrounded by a fainter region due to rays scattered by the film. In many cases this region was not, as one would naturally expect if the electron is regarded merely as a charged particle, one of uniformly diminishing intensity, but showed one or more rings with the main beam for their center. At first the rings were not very distinct and we suspected an optical illusion similar to that observed in previous positive-ray experiments.[2] It was found possible however to measure the rings photometrically, and they appeared as distinct inflections on the general curve of scattering. In the absence of any certain knowledge as to the crystalline state of celluloid, if any, it seemed natural to regard the rings as analogous to the

[1] Davisson and Germer, *Phys. Rev.*, 30, 722-740 (1927).
[2] G. P. Thomson, *Proc. Cambridge Phil. Soc.*, 23, 419 (1926).

halos formed by light passing through a cloud of small particles, as in Young's eriometer. The wave-length required was of the right order to fit de Broglie's formula, and the angular diameter of any ring was approximately inversely proportional to the square root of the voltage. In June 1927 a letter appeared in *Nature* describing these experiments,[1] two months after the preliminary account in the same journal of the experiments by Davisson and Germer described above.[2] Some delays were experienced in clearing up certain points of difficulty, and it was not

TABLE I.[3]

Plate	Voltage (P)	D_1 mm.	D_2 mm.	D_3 mm.	$D_1P^{\frac{1}{2}}/L$	$D_2P^{\frac{1}{2}}/L$	$D_3P^{\frac{1}{2}}/L$
March 16 (1)	9,800	12	—	—	54.4	—	—
March 19 (2)	10,800	10.6	—	—	57.5	—	—
March 15 (2)	14,800	9	18.4	—	54.5	112.0	—
March 15 (3)	19,700	8.2	—	—	57.5	—	—
March 15 (1)	26,000	7	14	22.5	56.4	112.9	180.8
March 16 (2)	29,500	6.5	13.6	—	58.8	116.8	—
March 19 (1)	35,100	6.25	12.2	19.8	58	114	186.5
April 17	40,400	5.5	11.5	18.5	55.1	115.8	186.5
Mean	—	—	—	—	56.5	114.4	184.6

till a year later that a final account appeared,[4] only a day or two before Mr. Reid's tragic death in a motorcycle accident. The final results showed three rings, for each of which the diameter D and the voltage P were connected by the law $D\sqrt{P}=$ constant. This is, of course, a necessary result in any diffraction pattern formed by de Broglie waves, since $\lambda \propto P^{-\frac{1}{2}}$ if relativity is neglected. The quantity P was determined by measuring the field required to deflect the rays onto the hole in the diaphragm, the dimensions of the apparatus being known.

The ratio of $D_1 : D_2$ is almost exactly 1 : 2, that of $D_1 : D_3$ is rather less than 1 : 3, but other plates than those quoted

[1] G. P. Thomson and A. Reid, *Nature*, **119**, 890 (1927).
[2] Davisson and Germer, *Nature*, **119**, 558 ff (1927).
[3] *See* A. Reid, *Proc. Roy. Soc. London*, **A119**, 665 (1928).
[4] A. Reid, *Proc. Roy. Soc. London*, **A119**, 663 (1928).

above showed a closer approach to this ratio and it seems probable that the rings are three successive orders. It will, of course, be understood that in these and the following experiments, the angle of diffraction is so small, of the order of 2°, that we can write $\sin\theta = \theta$. Thus if L (Fig. 17) is the distance of the plate from the scattering body, and if the effect is regarded as equivalent to reflection from a Bragg plane of spacing d, we can write:

$$D/L = 2\sin 2\theta = 2N\lambda/d \quad \text{(approximately)} \qquad (4)$$

The spacing d, calculated from the above formula, had a mean value of 4.46×10^{-8}. This is close to the value found for the cross section of long-chain carbon com-

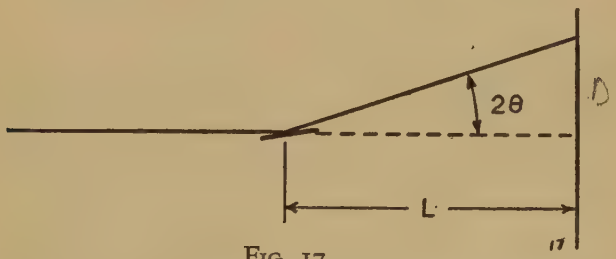


FIG. 17

pounds. These rings were always slightly blurred and it seems possible that they were really double, corresponding to two spacings close together. In one or two plates definite evidence of such doubling was obtained.

The films used had a thickness, as estimated by interference measurements and from measurements of their reflecting power for light, of the order 3 to 5×10^{-6} cm. They were made by flowing a drop of an amyl acetate solution of celluloid over the surface of a large dish of water and allowing the amyl acetate to evaporate. It is advisable to reject the first films formed as they will have picked up any dust particles which there may be on the water, and generally have holes in them.

METAL FILMS

The great disadvantage of experiments with celluloid is that its structure is unknown, and so no exact comparison with theory is possible. As soon as it seemed certain

that diffraction effects were being obtained with the electrons in celluloid films, I tried to make films whose structure was known, thin enough to give diffraction patterns. After several failures, films of aluminum and of gold were obtained which gave striking patterns. A little later platinum films were made and the results published in a letter to *Nature*[1] which appeared before the account of the experiments just mentioned, which were published in February 1928.[2]

The apparatus used was originally intended as provisional only, but it worked so well that only minor mod-

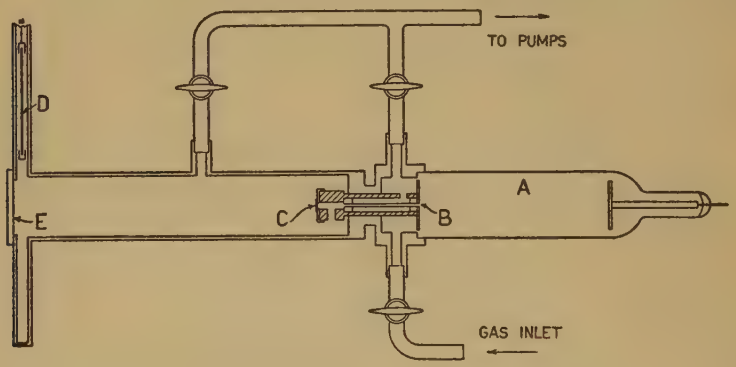
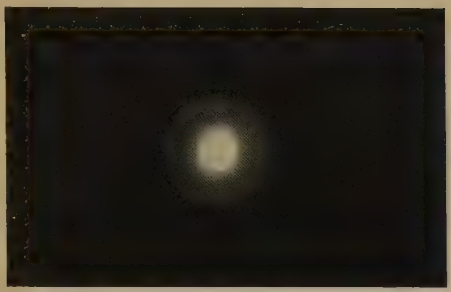


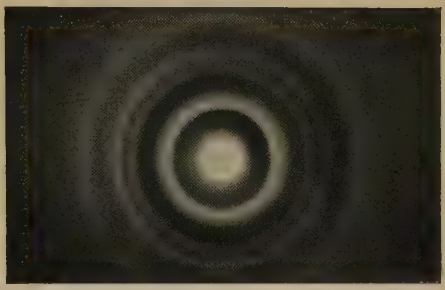
FIG. 18

ifications were made in the course of the work to be described. It is shown in Figure 18. Cathode rays (generated by an induction coil) in the tube *A* passed through the fine tube *B* of bore 0.23 mm. and length 6 cms., and struck a film mounted at *C*. The iron tube shown shaded in Figure 18 shielded *B* from magnetic effects. There was also a flat shield of soft iron round the neck between discharge tube and camera. The distance from *C* to the photographic plate *D*, when in position, was 32.5 cm. and *D* could be lowered in two stages by a magnetic release. This enabled two exposures to be taken on each plate, which was an advantage as it was difficult to estimate the best time of exposure to show up the pattern. At *E* was a willemite screen which could be used to examine the rays while the plate *D* was

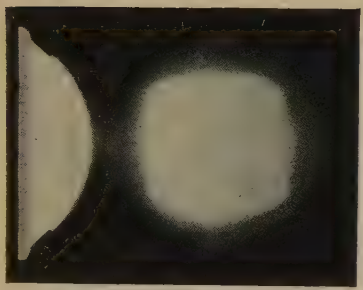
[1] G. P. Thomson, *Nature*, **120**, 802 (1927).
[2] *Proc. Roy. Soc. London*, **A117**, 600 ff. (1928).



a. Celluloid

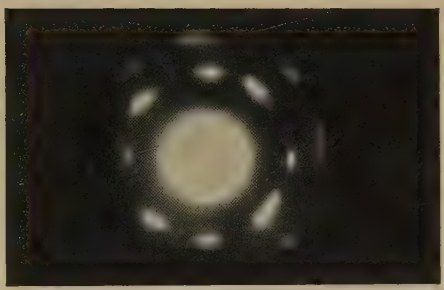


b. Gold

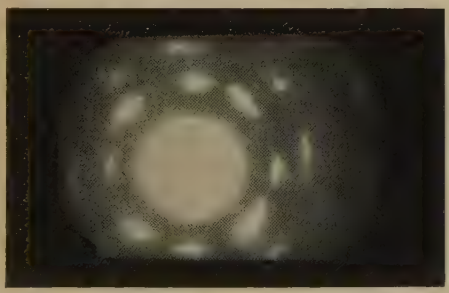


Courtesy Roy. Soc. London

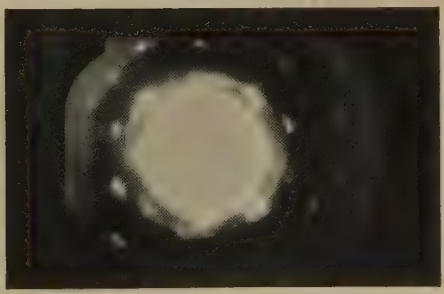
c. Aluminum



d. Aluminum



e. Aluminum



f. Aluminum

FIG. 19

still in the upper part of the camera. The camera was exhausted to a low vacuum, the gas coming through the fine tube from *A* being removed by a three-stage mercury vapor pump. The voltage of the discharge was measured as carefully as possible by means of a spark gap between 4 cm. aluminum spheres. A preliminary experiment of deflecting the rays by a magnet on their path between *C* and *E* showed that they were very nearly homogeneous, the spot on the plate deflecting as a whole except for a very faint tail.

The exposures used were from a few seconds up to a few minutes, depending on the intensity and voltage of the cathode rays used. A few experiments were made with celluloid films, which checked up well with Reid's results and showed that the spark-gap method of measuring potential was reliable.[1] It will be remembered that Reid determined the speed of his rays by the field required to deflect them onto a hole in a diaphragm, his measurements are thus independent of any assumption as to the behavior of the discharges.

Specimens of the results with gold, aluminum and celluloid are shown in Figure 19. It will be seen that in all cases the general effect is that of a series of concentric rings round the spot made by the undeflected beam. In some cases these rings are uniform round the circumference, in others the intensity is more or less concentrated in a series of spots on the circumference. It should be said at once that there can be no doubt that the whole pattern is due to cathode rays which have been deflected by the film. Thus in the absence of the film only the central spot is seen, and if a magnet is brought up between *C* and *E* (Fig. 18) the whole pattern is shifted together. In some cases, when bright enough, this can be seen by following the changes in appearance of the willemite screen when a magnet is brought near. In others, when the rings could not be seen on the screen, photographs were taken with a magnetic field between *C* and *D* strong enough to move the central spot—which could always be seen—through a

[1] An error of about 5 per cent in $\sqrt{P}$ was made in the first measurements owing to neglecting the fall of potential in the leads, valve, etc. This was corrected in a note on p. 661 of the paper in *Proc. Roy. Soc. London*, A119, (1928).

considerable distance. In all cases the pattern showed the spot at the center of the rings, showing that spot and rings had been deflected together. They thus are due to cathode rays of appreciably the same velocity.

A later quantitative investigation[1] showed that the agreement in velocity between the rays forming the rings and those in the central spot was exact to well within the experimental error, which was less than 1 per cent. The films in these experiments had numerous holes, so that the central spot was mostly formed by rays which had gone through without collision. The rings must therefore have been formed by electrons which had undergone elastic collisions only. Figure 20 shows photographs taken in the course of this research. The two sets of rings were obtained by reversing a magnetic field which deflected the rays between the film and the photographic plate. The spots in the center are the result of short exposures without the field and give the positions of the undeflected beams.

The general appearance of the rings immediately recalls that of the Hull-Debye-Scherrer X-ray rings in the case of gold, and a cross between these and a Laue pattern in the case of aluminum. It remains to see if the agreement is exact, and if so, if the value of the wave-length is that predicted by the de Broglie theory. Any diffraction pattern formed in directions making small angles with the original beam must fulfil the condition that its size is proportional to the wave-length causing it (see Equation 4). It is easy to show[2] that, if account is taken of relativity:

$$\lambda = h\sqrt{150/ePm_0}/(1+eP/1200m_0c^2) \qquad (5)$$

where P as before is the potential through which the electron has been accelerated, measured in volts, and the first power of eP/m_0c^2 is retained. The correcting term never exceeds 3 per cent in these experiments. The extent

[1] *Proc. Roy. Soc. London*, **A119**, 651ff (1928).

[2] We have $eP/300 = \frac{m_0c^2}{\sqrt{1-u^2/c^2}} - m_0c^2$, and $\lambda = \frac{h\sqrt{1-u^2/c^2}}{m_0u}$, eliminating u and approximating, the result follows. Note that $h/\sqrt{em_0} = 10^{-8}$, to the accuracy with which these quantities are known.

to which $D\sqrt{P}(1+eP/1200m_0c^2)$ is constant for a given ring of a given substance is shown by Table II.[1]

The measurements quoted are from my earlier paper,[2] but the result has been confirmed again and again. It holds good for all the metals with which these patterns have

TABLE II

Aluminum

Plate	Spark Gap mm.	P	D_1 cm.	$D_1\sqrt{P}(1+eP/1200m_0c^2)$
October 7 (3)	5	17,500	3.1	415
October 10 (2)	9.5	30,500	2.45	434
October 7 (2)	10	31,800	2.32	418
October 7 (4)	13	40,000	2.12	430
October 7 (5)	14.5	44,000	2.08	445
October 7 (6)	16.5	48,600	1.90	430
October 11 (1)	16.5	48,600	1.98	446
October 12 (2)	20	56,500	1.83	446
October 12 (3)	20	56,500	1.80	438
Mean	—	—	—	434

Gold

October 13 (1)	7.5	24,600	2.50	398
October 12 (4)	10	31,800	2.15	390
October 12 (5)	12.75	39,400	2.00	404
October 12 (6)	15.25	45,600	1.86	405
October 12 (7)	19	54,300	1.63	388
October 17	22	61,200	1.61	410
Mean	—	—	—	399

been obtained, *i.e.* gold, aluminum, platinum, silver, copper, lead, iron, nickel, tin, and also for several compounds. A slight apparent exception has been shown not to be real.[3] If not due to accidental errors it was probably caused by the rays not being quite homogeneous. We may thus take it that the variation of these patterns with the voltage of the rays is that required if they are caused by the diffraction of de Broglie waves.

[1] G. P. Thomson, *Proc. Roy. Soc. London*, **A117**, 603f (1928).
[2] *Proc. Roy. Soc. London*, **A117**, 600 ff (1928).
[3] G. P. Thomson, *Proc. Roy. Soc. London*, **A119**, 652 (1928).

Gold. The rings obtained with gold obviously resemble the patterns given by powders with X-rays. Gold crystallizes in face-centered cubes, for which the spacings are given by $d = a/\sqrt{l^2+m^2+n^2}$ where (lmn) are all even or all odd (see page 45). The diameters of the rings become:

$$D = \frac{2\lambda L\sqrt{l^2+m^2+n^2}}{a} \qquad (6)$$

The relative sizes of the rings in two early photographs with gold films are shown in the first two rows of Table III. The (220) ring is taken as standard. Below are some later measurements; in these the rays were made more uniform in velocity, and hence in wave-length, by placing two or three Leyden jars in parallel with the discharge tube. The increased homogeneity of the rays makes it possible to distinguish the rings corresponding to small spacings. Owing to the relative faintness of the outer rings it is not easy to make them show up well without overexposing the inner ones, which thus become difficult to measure accurately. All the possible rings are present up to $\sqrt{27}$, though $\sqrt{16}$ is always faint. The rings which should occur at $\sqrt{32}$ and $\sqrt{40}$ are masked by rings near them, but traces have been found by photometric measurement. Otherwise all possible rings up to $\sqrt{60}$ are present, though in several cases two or more rings are too close together to be resolved. In these cases a mean value has been calculated for $\sqrt{l^2+m^2+n^2}$, weighted to allow for the chances of the rings being formed in a random distribution of crystals. The later plates are a selection from a large number that have been taken for various purposes at different times, there are many others equally good. The agreement with theory is well within the errors of measurement of these rings, which range in diameter from a little over 1 cm. to about 6 cm.

Aluminum. Results for aluminum—also a face-centered cubic structure—are shown in Table III. In this case the "rings" consist of a number of separate spots (see Figure, 19 c, d, e, f,), but there is no difficulty in measuring the diameters of the circles on which they lie. It will be

TABLE III
Relative Diameters of Rings

Column	1	2	3	4	5	6	7	8	9	10	11	12
Plane indices (lmn)	(111)	(200)	(220)	(113) (222)	(400)	(331) (420)	(422)	(511) (333)	(531) (600) (442)	(533) (622)	(444) (700) (551) (640)	(642) (731) (553)
$\sqrt{l^2+m^2+n^2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{8}$	$\sqrt{11}$ $\sqrt{12}$	$\sqrt{16}$	$\sqrt{19}$ $\sqrt{20}$	$\sqrt{24}$	$\sqrt{27}$	$\sqrt{35}$ $\sqrt{36}$	$\sqrt{43}$ $\sqrt{44}$	$\sqrt{48}$ $\sqrt{49}$ $\sqrt{51}$ $\sqrt{52}$	$\sqrt{56}$ $\sqrt{59}$
$\sqrt{l^2+m^2+n^2}$ Weighted mean	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{8}$	$\sqrt{11.25}$	$\sqrt{16}$	$\sqrt{19.5}$	$\sqrt{24}$	$\sqrt{27}$	$\sqrt{35.4}$	$\sqrt{43.5}$	$\sqrt{50}$	$\sqrt{57.8}$
Gold:												
Oct. 12, 1927 (7)	$\sqrt{2.96}$	$\sqrt{4.08}$	$\sqrt{8.00}$	$\sqrt{11.2}$	missing	$\sqrt{19.3}$	—	—	—	—	—	—
Oct. 17, 1927	$\sqrt{3.02}$	$\sqrt{4.25}$	$\sqrt{8.00}$	$\sqrt{11.7}$	—	$\sqrt{19.9}$	—	—	—	—	—	—
Dec. 19, 1927 (3)	$\sqrt{2.95}$	$\sqrt{4.08}$	$\sqrt{8.00}$	$\sqrt{11.2}$	—	$\sqrt{19.5}$	$\sqrt{22.7}$	$\sqrt{26.6}$	$\sqrt{35.4}$	—	—	—
Feb. 25, 1929,	$\sqrt{2.96}$	$\sqrt{3.98}$	$\sqrt{8.00}$	$\sqrt{11.0}$	—	$\sqrt{19.5}$	$\sqrt{24.3}$	$\sqrt{27.8}$	$\sqrt{34.9}$	$\sqrt{43.1}$	—	—
Mar. 13, 1929,	$\sqrt{3.06}$	$\sqrt{3.9}$	$\sqrt{8.00}$	$\sqrt{11.0}$	—	$\sqrt{19.5}$	$\sqrt{24.1}$	$\sqrt{27.5}$	$\sqrt{35.0}$	$\sqrt{42.6}$	$\sqrt{50}$	$\sqrt{56.5}$
Apr. 12, 1929 (3)	—	—	$\sqrt{8.00}$	$\sqrt{11.25}$	$\sqrt{15.7}$	$\sqrt{19.4}$	$\sqrt{24.4}$	$\sqrt{26.7}$	$\sqrt{34.7}$	$\sqrt{43.5}$	$\sqrt{51.6}$	$\sqrt{58.4}$
Aluminum:												
	—	$\sqrt{4.00}$	$\sqrt{8.00}$	$\sqrt{10.9}$	$\sqrt{16.5}$	$\sqrt{20.4}$	—	$\sqrt{27.0}$	—	—	—	—
	—	$\sqrt{3.98}$	$\sqrt{8.00}$	$\sqrt{11.0}$	$\sqrt{15.7}$	$\sqrt{21.2}$	—	$\sqrt{27.8}$	—	—	—	—
	—	$\sqrt{4.02}$	$\sqrt{8.00}$	$\sqrt{10.9}$	$\sqrt{15.9}$	$\sqrt{19.4}$	—	$\sqrt{26.8}$	$\sqrt{36.0}$	—	—	—
	—	$\sqrt{4.00}$	$\sqrt{8.00}$	$\sqrt{10.9}$	$\sqrt{15.4}$	$\sqrt{19.2}$	$\sqrt{23.6}$	$\sqrt{27.4}$	$\sqrt{33.0}$	—	—	—
Platinum:												
	$\sqrt{3.00}$	$\sqrt{4.00}$	$\sqrt{8.00}$	$\sqrt{10.9}$	$\sqrt{15.3}$	$\sqrt{18.4}$	$\sqrt{24.0}$	$\sqrt{26.5}$	—	—	—	—
	$\sqrt{3.07}$	$\sqrt{4.01}$	$\sqrt{8.00}$	$\sqrt{11.3}$	—	—	—	—	—	—	—	—
	$\sqrt{3.04}$	$\sqrt{4.03}$	$\sqrt{8.00}$	$\sqrt{11.2}$	$\sqrt{16.4}$	$\sqrt{19.0}$	$\sqrt{23.4}$	$\sqrt{27.1}$	$\sqrt{35.0}$	—	—	—

seen that there is equally good agreement with the theory except for the curious omission of the $\sqrt{3}$ and probably $\sqrt{12}$, its second order. The explanation is as follows. The incomplete nature of the rings shows that comparatively few crystals are present in the area struck by the rays. Konobeievski[1] has shown, by X-ray methods, that in the thinnest aluminum foil the crystals are oriented with their (100) axes perpendicular to the foil. The films used in the above experiments were made by thinning down a piece of the thinnest leaf obtainable, in caustic potash. If the crystals in this case are orientated in the same way no reflection from a (111) plane will be possible, because the Bragg law requires the incidence to be only about one degree from grazing and no (111) planes will be present at so small an angle to the rays. If the orientation were absolutely exact and if the films were perfectly flat, no spots of any kind would be theoretically possible except those due to such planes as might make exactly the right small angle with the incident beam. It would be like trying to take a Laue photograph with monochromatic X-rays. Actually the various small imperfections make it possible to obtain reflections from all the planes which pass through the crystal axis. It is generally found that an intense spot has another diametrically opposite it on the same ring. The piece of crystal is sufficiently warped for the rays to fall sometimes on one side of the plane and sometimes on the other at a sufficient angle to give the reflection. In one case the specimen used appeared to be almost a single crystal in the region used. The inner circle (200) reduced to four spots at the corners of a square, while the next (220) took the same form with the difference that the diagonals of the two squares make an angle of 45° with each other (Figure 20, c). Since the (220) planes are at 45° to the (200) planes this result is in exact agreement with what would be expected according to the theory. The orientation is usually far from perfect, and the range is sufficient to allow such planes as (311), (331) and (511) to give reflections. The relatively large

[1] Konobeievski, *Z. Physik*, **43**, 741 (1927).

ratio of the indices in these planes implies that they make a fairly small angle with a (100) direction. It will be noticed that (422) seldom appears while (400), which is very weak for gold, occurs regularly.

Inclined Films. A few experiments were made with films inclined to the rays, the angle between the film normal and the rays being about 30°. If the crystals of the film are arranged quite at random, no change should be produced by inclining the film;[1] but if the crystals have dominant directions with regard to the plane of the film, changes will be produced in the relative intensities of different parts of the same ring, and the different rings as a whole.

A silver film, prepared by Ironside,[2] showed marked difference in the brightness of different parts of the (200) ring when inclined, though when the film was normal to the rays the ring was of uniform intensity. The brightest parts were at the ends of a diameter parallel to the axis about which the film had been turned. This is what would be expected if there was a tendency for the crystals to be set with one axis normal to the film. The only planes that can reflect the rays are those which make a small angle with them, since the wavelength is small compared with the spacing, and the only (200) planes which would fulfil this condition would be those whose normals nearly coincided with the line about which the film had been turned. That all the crystals are not placed in this way is shown by the fact that the (111) ring appears with the film in the usual position. This ring in the inclined film is brightest on the diameter at right angles to that for the (200) ring, and as the two rings are close together the whole has an elliptical appearance.[3] For an aluminum crystal which showed, in the normal position, a number of spots on the (200) ring, a pair on the diameter parallel to the axis of turning of the film showed strongly. A few other spots were, however,

[1] See, however, page 98.

[2] R. Ironside, *Proc. Roy. Soc. London*, **A119**, 668 (1928).

[3] *See* G. P. Thomson, *Proc. Roy. Soc. London*, **A119**, Plate 12A, fig. 3 (1928).

visible on the ring; the orientation of the crystals with their axes perpendicular to the film therefore is not perfect.

Platinum. Some very thin platinum leaf showed results intermediate between those of gold and aluminum. The rings at first consisted of a large number of spots, but not enough to make them quite continuous. After being laid aside for a few weeks the same film showed continuous arcs extending over about 60° (Figure 20, b). It is possible that this was a slightly different part of the film, but as several plates were taken in each case, with consistent results, it is more likely that a change had been produced in the film, perhaps caused by strains due to thermal expansion of the pierced aluminum disk on which it was mounted. To produce the later pictures the crystals must have had preferred directions, though the orientation is by no means exact, as shown by the length of the arcs. The pattern shows a clear 4-fold symmetry.

Copper, Nickel. Ironside[1] found with copper films, made by thinning down beaten copper, a tendency to orient with a (100) axis perpendicular to the film. The (111) ring was absent. Most of the other experiments have been made on films formed by cathodic spluttering, these show uniform rings like those of gold. In the great majority of cases the sizes of the rings are in the ratio demanded by the known crystal structure. Nickel is exceptional in showing an hexagonal structure instead of a cubic one (see p. 78). One or two other apparent exceptions are dealt with below under the metal to which they refer.

ABSOLUTE VALUE OF THE WAVE-LENGTH

The final stage in the verification of de Broglie's theory is the comparison of the absolute value of the wave-length with that given by experiment. From each ring of each picture a separate wave-length could be deduced and compared with de Broglie's formula. But as the wave-length varies with the speed in the way we have shown, a better method is to assume the theoretical formula and use it to calculate "*a*", the size of the unit cube, by means

[1] R. Ironside, *Proc. Roy. Soc. London*, **A119**, 668 f (1928).

of Equation (6). The mean of all the plates can then be taken and compared with the value found by X-rays.

Where two measurements are given in Table IV, they refer to plates taken with different apparatuses. The table shows agreement within 2 per cent in all cases except in one set of measurements of gold, and in most cases the error is about 1 per cent. This is well within the error of experiment.

TABLE IV

Size of the Unit Cube, a.

Metal	Measurements	
	X-ray	Cathode ray
Aluminum	4.046×10^{-8}	$\left.\begin{matrix}4.06\\4.00\end{matrix}\right\} \times 10^{-8}$
Gold	4.06×10^{-8}	$\left.\begin{matrix}4.18\\3.99\end{matrix}\right\} \times 10^{-8}$
Platinum	3.91×10^{-8}	$\left.\begin{matrix}3.88\\3.89\end{matrix}\right\} \times 10^{-8}$
Lead	4.92×10^{-8}	4.99×10^{-8}
Iron	2.87×10^{-8}	2.85×10^{-8}
Silver[a]	4.079×10^{-8}	4.11×10^{-8}
Copper[a]	3.60×10^{-8}	3.66×10^{-8}
Tin (white),[a] spacing of (200)	2.91×10^{-8}	2.86×10^{-8}

[a] Measurements by Ironside, *loc. cit.*

The agreement is thus entirely satisfactory and we are driven to suppose that the electrons form diffraction patterns just similar to those which would be produced by waves of $\lambda = h/mu$. All we have had to assume, in deducing these results, is that each atom acts as a scattering center and that the scattered waves are coherent in phase and wave-length with the incident train. This last requirement means that there must be no loss of energy by the scattered electrons, which we have seen is experimentally verified. Besides these elastic collisions there are, no doubt, also inelastic ones. These will cause the continuous

background which is always observed between the rings. Since the whole crystal influences the diffracted beam, the scattering in it, if it is regarded as due to a collision of the electron at all, must be considered to be one with the whole crystal. As this is of practically infinite mass there need be no transference of energy. If, on the contrary, the ray were scattered by another free electron, we should have $u - u' = u \sin^2\theta$, where u, u' are the initial and final component velocities along the original beam, and θ is the angle through which the *relative* motion has turned. For small angles $\sin\theta = 2 \sin\phi$, when ϕ is the angle of deflection of the ray. Thus $(u-u')/u = 4 \sin^2\phi$. For the rings considered ϕ is about 0.04, thus $(u-u')/u$ is nearly 1 per cent, and should have been detected. The energy given to the free electron would be $(0.04)^2$ of the original energy. This would be of the order 100 volts. Probably a collision with a bound electron would lead to much the same result if this energy were sufficient to ionize, as would be the case for the outer electrons. Thus the experiment serves to confirm the expectation that, if the scattering is regarded as a collision phenomenon, the collisions must be regarded as being with the crystal, or at least the atoms, rather than with electrons.

RESOLVING POWER

It is of interest to consider what can be deduced as to the nature of the waves and crystals from an observation of the width of the rings, as shown, for example, by finding whether two rings close together can be seen as separate.

The width of the rings is due to a variety of causes—the finite size of the original beam, the limited extent of the several crystals, and the lack of homogeneity of the rays; but it will also be affected by the number of coherent waves that form the train associated with each electron. The last two causes are closely connected, and on some views are different aspects of the same effect.

In practice the first cause is probably the largest, at least when a condenser is used, but observations of resolving power will give a lower limit to the size of the crystals, and to the number of waves in a train.

If the beam is considered infinitely fine and the number of elements in the crystal infinite, the resolving power can be calculated in terms of the number of waves as follows. Assume a group of waves for which the intensity is constant from $\lambda - \Delta\lambda$ to $\lambda + \Delta\lambda$, and vanishes outside this range. If p is the order of the reflection $p\lambda = 2d \sin\theta$, and if θ_1, θ_2 are the values of θ for the centers of two rings which are just resolved, $2p\Delta\lambda = 2d(\theta_2 - \theta_1)\cos\theta = 2d(\theta_2 - \theta_1)$, approximately. The number of waves in the train can be found as follows: suppose they are all in phase at $x = 0$, then at $x = r\lambda$ the displacement will be

$$\int_{-\Delta\lambda}^{\Delta\lambda} \cos\frac{2\pi x}{\lambda + t}\,dt = \frac{\lambda^2}{2\pi x}\left[\sin 2\pi r\left(1 - \frac{t}{\lambda}\right)\right]_{-\Delta\lambda}^{+\Delta\lambda}$$

if $\Delta\lambda/\lambda$ is small. For r an integer this becomes $\frac{\lambda}{\pi r}\sin 2\pi r\frac{\Delta\lambda}{\lambda}$. Thus the amplitude vanishes when $2\pi r\frac{\Delta\lambda}{\lambda} = \pm\pi$, and $2r$, the total number of waves on both sides of the origin, is $\lambda/\Delta\lambda$. Thus $2r = p\lambda/d(\theta_2 - \theta_1) = 2\theta/(\theta_2 - \theta_1)$.

In these experiments the rings $\sqrt{24}$ and $\sqrt{27}$ were easily resolved, $\sqrt{11}$ and $\sqrt{12}$ barely in very favorable circumstances; but it is safe to say that they would have been fully resolved but for the finite width of the original beam. This gives $2r = 2\sqrt{11}/(\sqrt{12} - \sqrt{11}) = 48$. In all probability the number was larger, as the width of the beam would by itself account for most of the observed width of the diffraction rings.

This result means that the wave train must extend in depth a distance of about 4×10^{-8} at the least, or more than the diameter of an atom. Even a larger limit can be assigned to its lateral extension. Suppose the incident waves perfectly monochromatic, and consider the width of the rings as due to the fact that the crystals are not infinite in extent. Consider a spot due to reflection from a crystal plane which, since the angles are small, must be nearly normal to the film (Fig. 21). The thickness t of the film $\sim 10^{-6}$. The beam reflected from one such plane has

a breadth $\sim 10^{-6}\sin\theta$. Such a beam if left to itself will spread by diffraction, the half-width ϕ being given by $\phi 10^{-6}\sin\theta \sim \lambda$. Now $\sin\theta \sim 1/50$ and $\lambda \sim 10^{-9}$, hence $\phi \sim 1/20$ and is greater than θ, so that no well-defined beam is possible. Hence the beams depend for their fineness, even if the film were a single crystal, on the interference from successive Bragg planes. The rays reflected from such planes (Fig. 22) can be regarded each as a single ray coming

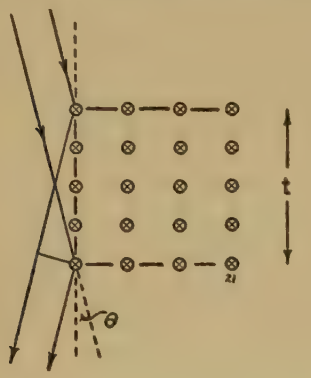


FIG. 21

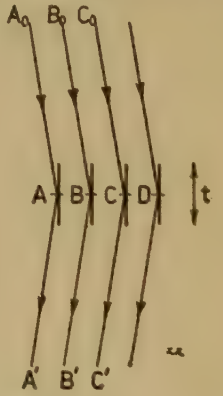


FIG. 22

through the center of the plane from the image of the source. This is practically equivalent to a plane grating, at nearly normal incidence. The angular distance between the maximum and the first minimum is $\delta\theta = \lambda/Nd$ where N is the number of planes. Now if $\sqrt{11}$ and $\sqrt{12}$ of diameters D_{11} and D_{12} are just resolved $\delta\theta = (D_{12}-D_{11})/2L = \lambda\left(\frac{1}{d_{12}}-\frac{1}{d_{11}}\right) = \lambda(\sqrt{12}-\sqrt{11})/a$. Therefore, the width of the beam, which is approximately Nd, must be at least $a/(\sqrt{12}-\sqrt{11}) = 7a$. Thus the beam must extend over about 30Å and cover a large number of atoms.

In the above experiments the current was such that there would seldom be more than one electron in the film at once, so that we cannot regard this wide beam as the result of some agreement in phase between the waves of different electrons. One is driven to suppose that each electron has a wave system at least 4Å from back to front, and 30Å in the wave front.

It perhaps needs explanation how it is possible still to get sharp rings with a number of crystals if the reflection from each plane is as diffuse as the above calculation shows it to be. One would expect that, regarding each crystal as nearly equivalent to a plane grating, the spectra due to a large number of such gratings arranged at all angles of incidence would be very diffuse; for the deviation due to a grating depends on the angle of incidence. The possibility depends on the smallness of the angles. For a plane grating, if θ_1 is the angle of incidence and θ_2 that of diffraction, $b(\sin\theta_1 - \sin\theta_2) = n\lambda$. Now if θ_1, θ_2 are small this is $\theta_1 - \theta_2 = n\lambda/b$, but $\theta_1 - \theta_2$ is the deviation, which is thus independent of the attitude of the grating provided θ_1 is small. When θ_1 ceases to be small the situation is saved because there really are more than one layer of atoms in the thickness t of the small crystal, and in a direction which differs greatly from AA' (Fig. 22) the rays from different atoms in the plane through A will show destructive interference, which will be all the more marked because the rays are no longer near grazing incidence.

EXPERIMENTAL DETAILS

For the work with magnetic deflection described on page 62, a shorter camera was used, the distance from plate to film being 24.8 cm. instead of 32.3 cm. The magnetic field was produced by two large coils 46.5 cm. in diameter, placed as nearly as possible in the Helmholtz arrangement with their common axis horizontal and perpendicular to the beam of rays. The soft iron shield between the camera and discharge tube was removed. In all the later experiments two or three Leyden jars were connected across the discharge tube. This greatly improves the homogeneity of the rays. In the exposures taken with the magnetic field it was found that the parts of the pattern towards the original center were clearer than without the magnetic field, while those on the other side were more blurred. This effect is exactly analogous to the achromatizing of Newton's rings by viewing them through a prism, and is caused by the rays being not quite homogeneous even with

the condenser. The times of exposure in these, as in the earlier, experiments varied from a few seconds to a few minutes depending chiefly on the voltage used.

Preparation of Films

The films used in the first experiments were prepared by taking the thinnest obtainable commercial metal leaf, and reducing it still further with reagents—aqua regia in the case of gold and caustic potash in that of aluminum. This process is a difficult one and involves a large percentage of losses. It is necessary to wash the films several times to remove traces of the reagent, and it was sometimes found necessary to use a series of solutions graded so that there was no great difference between the surface tension of any two, as most of the breakages occur from surface tension forces. The films so formed always have holes, and under the miscroscope look almost like a piece of lace. It is thus practically impossible to estimate the effective thickness. In the case of platinum the first successful films were made by spluttering the platinum onto glass and removing the films with hydrochloric acid. These films were too thin to stand alone and always broke on mounting, so they had to be floated onto a backing of the thinnest celluloid film and the composite film used. These composite films gave the rings to be expected of platinum but they were not very sharp. This is owing no doubt to the additional scattering produced by the celluloid, which is made worse since some of the celluloid rings nearly coincide with the platinum ones. The rings formed in this way were quite continuous. After a partially successful attempt to make films by beating down foil and reducing in aqua regia, it was found that sufficiently thin leaf could be obtained commercially to give good rings without further treatment. The results obtained in this way have been described above. All these films were mounted on aluminum disks about 1 cm. in diameter pierced with a 1 to 2 mm. hole across which the film is stretched.

Silver. Films of silver were prepared by Mr. Ironside, for his experiments, by chemical deposition on glass with a

silvering solution and removal of the film; and also by reducing silver leaf in nitric acid. They gave results in good agreement with the theory.

Copper. Copper films were prepared by reduction of thin leaf in nitric acid. These showed some abnormalities in the ring patterns which they gave. In all, seven rings were obtained, of which the first soon disappeared and is probably due to some organic substance; its spacing is about that of celluloid. The fourth, sixth and seventh rings agree well with what is expected of copper. The fourth being due to the (200) planes, the sixth to the (220) and the seventh to the (311). The second, third and fifth rings correspond to nothing in the copper structure. In appearance they differ from the copper rings in that the latter consist of circular arcs while these are continuous. Ironside identified them as being due to cuprous oxide. The third and fifth rings corresponding to (111) and (220) planes, respectively, of the face-center lattice formed by the copper atoms, while the second ring is due to the (110) spacing of the cube of the body-center lattice formed by the oxygen atoms. These three rings gradually increase in strength as the film grows older, pointing to a steady process of oxidation.

Tin. Films of tin were prepared by beating out tin foil and thinning down in acetic acid. The films were fragile and none gave more than two rings but, as seen from Table IV, these give a correct value of the grating constant.

Spluttered Films

I have been helped by a suggestion made by F. Jolliot who pointed out to me the advantages of cellulose acetate as a base on which to splutter. The technique as now developed is as follows. A solution of pure cellulose acetate in acetone is clarified by filtering. Some of the solution is poured on to a clean glass plate, allowed to solidify, and stripped off; this is done in order to remove specks or dust particles from the plate. When the plate has warmed up again to room temperature, enough solution is poured on to form a film rather too thick to show interference colors, but of that order. Round the edges of

this film more solution is applied with a paint brush as the first lot dries. In this way a kind of picture frame is built up round the thin center portion, which can be lifted off by means of the frame. It is then placed in a bell jar 3 or 4 cm. below a cathode of the metal to be spluttered. The spluttering is done with a current of 1–3 milliamps. with a dark space of about 1 cm. A thermionic valve is used to prevent back current from the induction coil. In most cases residual gas was used, but sometimes the gas was 99 per cent argon. In order to obtain films free from holes it was found necessary to make the cellulose acetate films, and transfer them to the bell jar, in a carefully sealed fume cupboard through which a stream of filtered air was drawn. Otherwise minute dust particles settled on the surface of the cellulose acetate and interrupted the continuity of the metal film. When the spluttering has given a sufficient deposit—5 minutes to an hour, the time being judged from the appearance of the surface—the composite film is removed from the bell jar and the cellulose acetate dissolved off in a bath of acetone. The metal film drifts away in the liquid, and must be washed by transferring it in a glass spoon to clean acetone; four successive washings in separate dishes of acetone are needed to remove all traces of the cellulose acetate. A portion of the metal film is then caught on an aluminum disk pierced with a hole 1–3 mm. in diameter. The film is manoeuvred over the hole and sticks to the disk when it is removed from the acetone and dried. With practice the proportion of losses is suprisingly small, considering that the thickness of the film is of the order of 10^{-6} cm. as determined from their optical density.

A variant of this method was to substitute a polished rocksalt crystal for the cellulose acetate. This has previously been used by Rupp (see p. 78) as a basis for his evaporated films. The spluttering in most cases was done in a stream of argon originally 99 per cent pure and further purified by standing for an hour over a hot tungsten filament. The rocksalt was removed by solution in brine. Films formed in this way were never as strong as those from cellulose acetate, they were difficult to mount and

were never obtained free from holes. In some cases, however, they gave markedly better rings. However prepared, the films actually used were always highly transparent, sometimes almost invisible by transmitted light, in other cases showing appreciable color. They could always readily be seen by light reflected at oblique incidence. They were too thin to show interference colors.

Gold. This method has been most successful with gold films, but a curious difference in color was noticed between the films usually obtained, which were pale green by transmitted light, and some exceptional ones which were a pinkish purple. The latter gave quite measurable rings of the same size and arrangement as the former but they were never really good. The pinkish films were generally found when the spluttering had been slow, and it seems possible that they contained layers of gas inclosed in the gold.

Silver. Silver gives satisfactory films by this method, but not quite so good as gold, the greatest number of rings visible being six. The films are pale orange by transmitted light.

Lead. This element gives small rings owing to the large size of the crystal cube (4.92×10^{-8}). The rings were not very sharp and the (111) and (200) rings were not resolved. These films were always tightly stretched over the aluminum mount while the gold films usually showed folds. It seems possible that the lead film may have been stretched beyond the elastic limit, and the crystal lattice deformed. The rings are in good agreement with the theory.

An interesting effect was observed when films were made from lead sputtered on to rocksalt in argon. The temperature was high enough to begin to melt the lead cathode. The films were very brittle, but one was mounted. It gave excellent rings, very narrow and persisting even at voltages as low as 6,000, but showing quite a different pattern from that of the familiar face-centered cube. The chief spacings calculated from four plates are as follows:

Spacing in Å units:	About 4.2	2.88	2.59	2.23	1.68	1.48	1.29–1.25	1.11–0.99
Character of ring:	Uncertain, hardly distinguishable from central spot.	faint	strong	diffuse	moderate	moderate	just resolved	faint

These spacings do not fit any probable structure for the metal and are probably due to one of its compounds, perhaps $PbCl_2$.

Iron. A number of films of this metal were prepared on cellulose acetate. They were very transparent and practically colorless by transmitted light. The rings were not very good but the measurements agree satisfactorily with the body-centered cubic structure found by X-rays; the rings corresponding to $\sqrt{6}$ and $\sqrt{8}$, however, were not resolved. A film spluttered in argon on rock salt showed two rings which do not fit the structures of iron, and one of the cellulose films showed the same rings together with the normal iron ones. With only two rings it is not possible to determine the nature of the substance causing the effect.

Nickel. Nickel films obtained by cellulose acetate gave very poor rings not measurable with certainty; spluttering on rock salt crystals gave very brittle pale brown films. These gave good rings, but their arrangement could be seen at a glance to be quite different from the familiar face-centered cubic pattern, though this is given in Table V as being the structure of nickel, and the experiments of Davisson and Germer with large crystals, and of Rupp with thin films, have confirmed the result by electron diffraction. Further investigation showed that the rings were in excellent agreement with a close-packed hexagonal structure for which "a" is 2.474×10^{-8} and "c" is 4.06×10^{-8}. This gives a density of 8.86 which agrees with the usual value of 8.9. This is as it should be, for both types of structure are equally close-packed. Thus nickel agrees with cobalt in crystallizing in both the systems of close-packing.

RUPP'S EXPERIMENTS

Dr. E. Rupp has made a series of experiments on the diffraction patterns formed by slow electrons of 150–290 volts energy going through thin metal films.[1] He, also, finds a series of rings whose sizes agree, within a few per cent, with the simple theory. His results are summarized in Table V.

[1] E. Rupp, *Ann. Physik*, 85, 981 (1928).

In this table λ is the wave-length calculated from Equation (1) and $\bar{\lambda}$ is the wave-length calculated from the observed size of the rings. Many of the rings were diffuse and some faint. The relative sizes of the rings agreed with the crystal structure to about 5 per cent. In a later paper Rupp states[1] that the films were erratic in

TABLE V

E. Rupp's Results with Slow Electrons Traversing Thin Metal Films

Metal	Crystal Form	Voltage	Rings Observed	$\lambda/\bar{\lambda}$
	Cubic			
Al	Face-centered	180–185	(111), (200), (311)	1.05
Ag	"	150	(111), (200), (220)	1.06
	"	180	(111), (200), (220), (311)	1.05
	"	220	(111), (200), (220), (311)	1.04
	"	280	(200), (220), (311) (222), (400), (331), (420)	1.03
	"	320	(111), (200), (311), (222)	1.01
Cu	"	280	(111), (200), (220)	1.03
Au	"	290	(200), (220), (311), (222)	1.03
Pb	"	280	(111), (200), (311)	1.02
Ni	"	220	(111), (200)	1.05
Cr	Body-centered	290	(110), (111)	1.04
Sn	*Tetragonal*	280	One ring, probably multiple	?
Zn	*Hexagonal*	280	(0002), (10$\bar{1}$0) (10$\bar{1}$1) and (10$\bar{1}$3) (11$\bar{2}$0) unresolved	1.00

behavior, many failing to give the rings. There seemed to be no correlation between the optical density and the behavior of the rings in the experiments. The films were made by evaporation of the metal *in vacuo* onto a polished crystal of rock salt which was then dissolved away. The order of thickness was 10^{-6}. I have tried[2] to repeat the experiments with films made by spluttering, but without success. When my films were free from holes I did not

[1] Rupp, *Ann. Physik*, (5)1, 773 (1929).

[2] G. P. Thomson, *Proc. Roy. Soc. London*, A125, 352 (1929).

even get a definite spot for the undeflected beam. In view of their erratic behavior it seems probable that some of Rupp's films had patches much thinner than their average thickness, and that it is these alone which are effective in producing diffraction rings. Rupp regarded the difference between λ and $\bar{\lambda}$ as explained by the metals having a refractive index for the electrons slightly greater than unity, but there seems no theoretical justification for the formula used. The question is discussed more fully in Chapter V. In any case, Rupp states that the effect is near the limit of accuracy of the measurements.

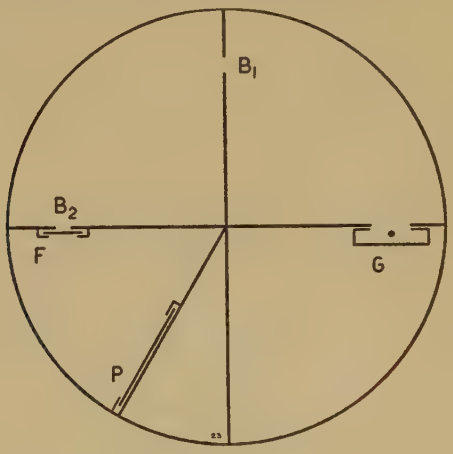


FIG. 23

EXPERIMENTAL DETAILS

The apparatus used was similar to that used by Ramsauer in his work on the free paths of electrons in gases. It is shown in Fig. 23. Electrons from a thoriated tungsten filament at G are accelerated by a potential difference between G and the case. They are bent into a circle by a uniform magnetic field perpendicular to the plane of the paper, and pass through diaphragms B_1 and B_2. The thin film is at F, and the electrons which pass through it strike a photographic film at P. This was coated with oil to make it sensitive to slow electrons. The exposures were long, up to 40 hours. Since the electrons follow a curved path after leaving the films, it is difficult to find the effective

distance, L, of the photographic film from the scattering point in order to use Equation (4) on page 59. This quantity was measured by bending a piece of wire into a circle and finding the curved length which reached from F to a point on the ring to be measured. Rupp then takes (in our notation) $2\theta = D/2L$ where $D/2$ is the distance of a point on the ring from the central spot. This measurement of L is probably the least certain part of the experiment. The mean radius of the circular path of the rays was 2.8 cm.

In a second paper Rupp measures the scattered electrons electrically.[1] A Faraday cylinder with an annular opening is placed behind the film, and the current to it measured for varying voltage of the rays. The electrons were incident normally on the film, and there was no magnetic field. If the voltage is such that a diffraction ring coincides with the opening of the Faraday cylinder one would expect an increase of current, and this is found to occur. Well-marked maxima of the curve—current to Faraday cylinder against electron voltage—were found for nickel, aluminum, and silver. The voltages were in agreement with the theory for the (111) ring of nickel and the (111) and (200) for aluminum and silver. In addition there were some fainter maxima which Rupp ascribed to planes such as (100), which do not ordinarily give reflections, and to impurities. Their significance seems doubtful. Chromium gave a faint ring corresponding to (110). The voltage ranged from 50 to 500, the chief maxima being near 300. In these experiments there was a back voltage of 9/10 of the total on the collector to stop slow electrons, as in Davisson's and Germer's experiments. By varying the back voltage, Rupp was able to show that the rings contain a large proportion of electrons of nearly the full energy of the beam, thus confirming the results of Davisson and the author.

Tartakovsky[2] had previously used the same method with a thin piece of aluminum foil and electrons of 200–1360 volts energy. He found maxima of current to the annular collector at voltages corresponding to rings

[1] Rupp, *Ann. Physik*, (5)1, 773 (1929).

[2] Tartakovsky, *Compt. rend. acad. sci. U.R.S.S.*, 1928, 14.

formed by reflection from (100) and (111) planes as well as some unidentified. It is difficult to see how the former plane can give a reinforced beam. There is no sign of such a ring in any of my photographs and if the effect exists it seems to be confined to low-speed electrons (see, however, p. 101). It may possibly be due to a compound.

KIKUCHI'S RESULTS

Some very beautiful and remarkable results have been obtained by S. Kikuchi with thin films of mica.[1] He used the apparatus shown in Figure 24. Cathode rays from the

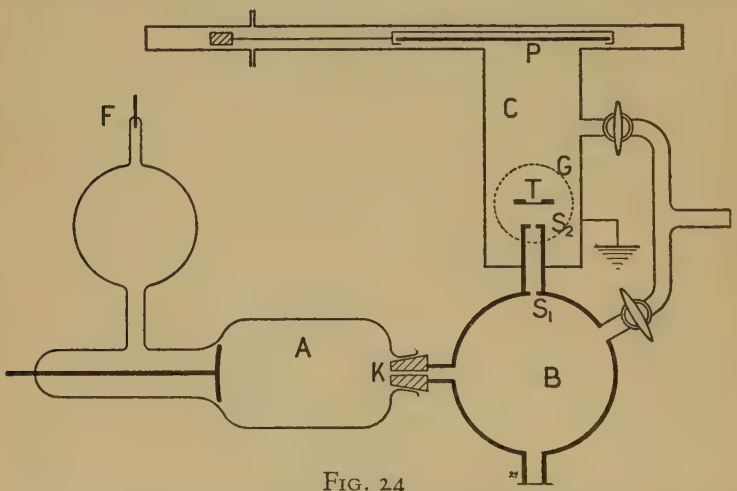
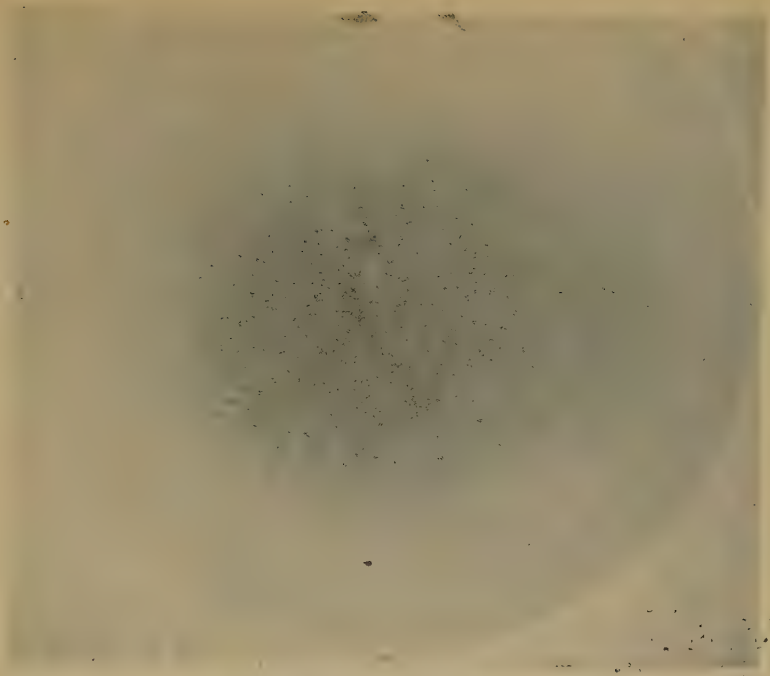


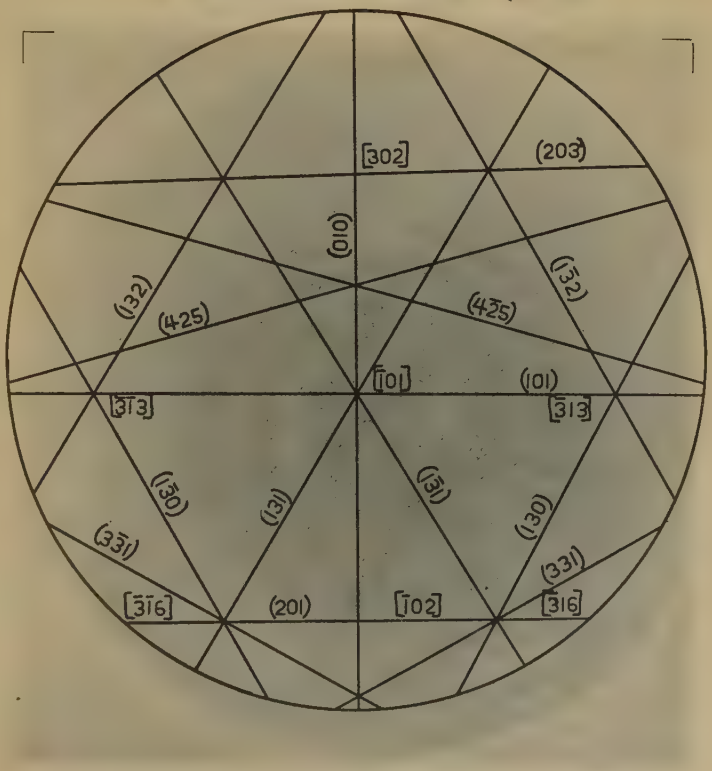
FIG. 24

discharge tube *A* were made uniform in velocity by being deflected in a magnetic field through the slits S_1, S_2. The stray field between the slits was neutralized by subsidiary coils. The mica is placed at *T* and can be rotated about an axis perpendicular to the paper by the ground joint, *G*. It can also be moved in its own plane if required. The photographic plate is at *P*. The voltage used ranged from 10,000 to 85,000. He determined the velocity of the rays from the current in the coils producing the magnetic field. This was calibrated in an original manner by replacing the mica by a thin aluminum film and observing the sizes of the electron diffraction rings for various currents in the coils.

[1] S. Kikuchi, *Proc. Imp. Jap. Acad.*, 4, 271, 275, 354, 471 (1928); and *Japanese Journal of Physics*, 5, 83 (1928).



a. Mica, N-pattern. $\lambda = 0.047$ Å (×1.6)



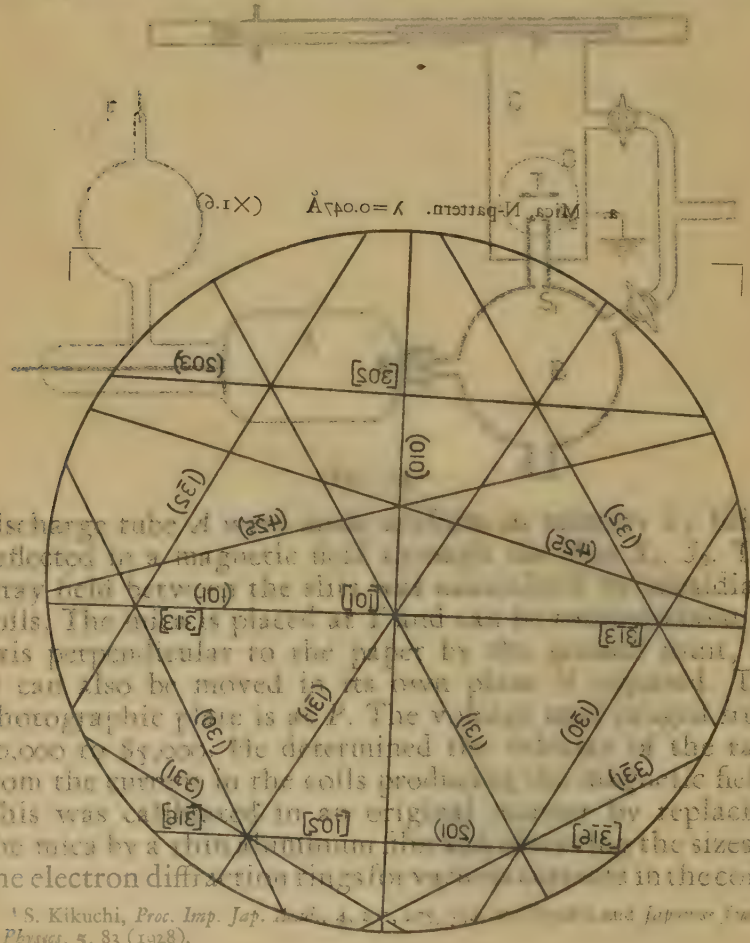
b. Mica, L-pattern. $\lambda = 0.6477$ Å (×1.55)

Fig. 15

formed by reflection from (100) and (111) planes as well as some secondary. It is difficult to see how the former planes can give a reinforced beam. There is no sign of such a ring in any of my photographs and if the effect exists it seems to be confined to low-speed electrons (see, however, p. 90). It may possibly be due to a compound.

KIKUCHI'S RESULTS

Some very beautiful and remarkable results have been obtained by S. Kikuchi with rock salt of mica.[1] He used the apparatus shown in Figure 24. Cathode rays from the

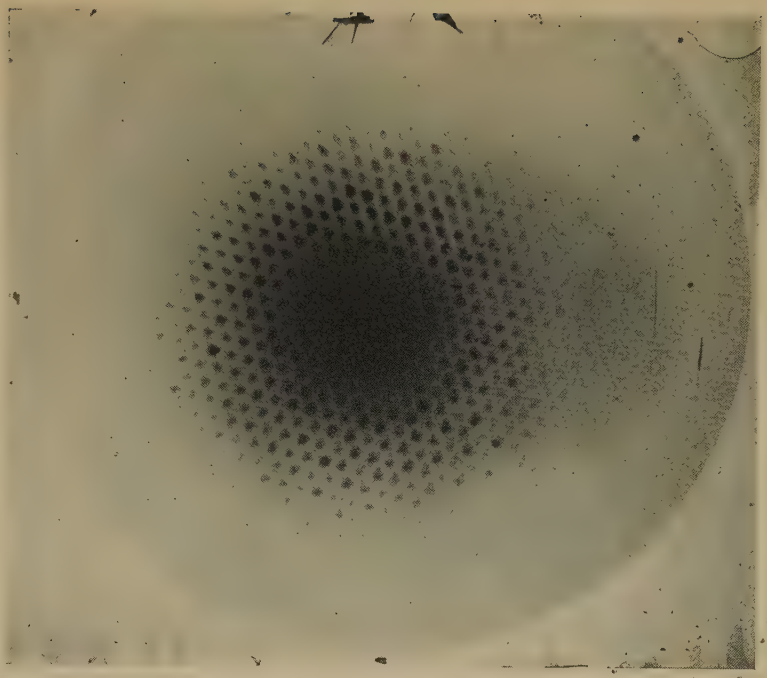


a. Mica, N-pattern. $\lambda = 0.0472$Å (×1.6)

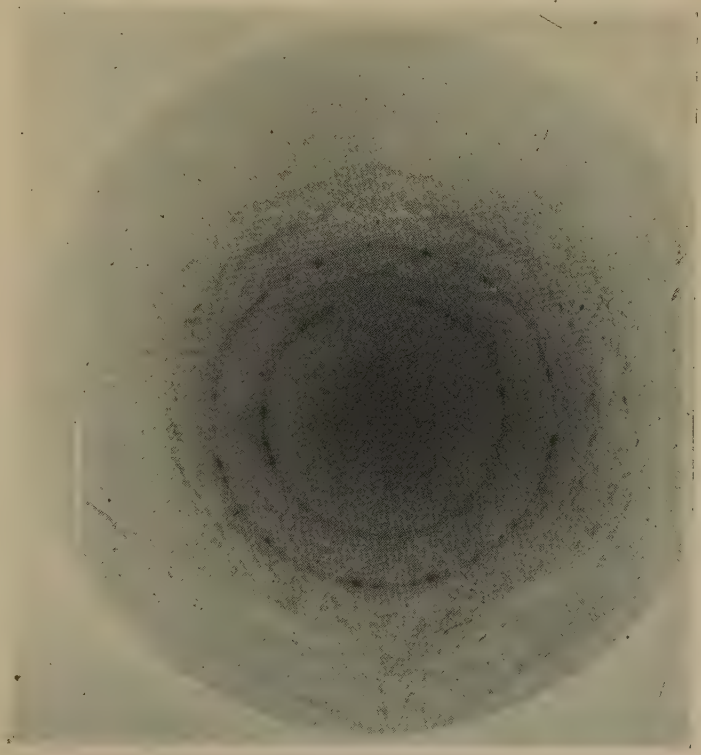
b. Mica, L-pattern. $\lambda = 0.0477$Å (×1.55)

FIG. 25

[1] S. Kikuchi, *Proc. Imp. Jap. Acad.* 4, [illegible] and *Japanese Journal of Physics*, 5, 83 (1928).



a. Mica, N-pattern. $\lambda = 0.047$Å (×1.6)



b. Mica, L-pattern. $\lambda = 0.0477$Å (×1.55)

FIG. 25

Three types of diffraction were found, depending on the thickness of the mica film. The patterns with the thinnest films (thickness of order 10^{-5} cm.) showed a net-like pattern of spots arranged in three sets of parallel lines at 60° to each other (Figure 25, a) (so-called "N-pattern"). With films thick enough to show interference colors this is replaced by the "L-pattern" (Figures 25, b, and 26,a) consisting of spots resembling Laue spots; there are also black and white lines. These latter persist when the thickness is further increased and form the "P-pattern" which can be seen, though faintly, even when the film is so thick that the central spot has disappeared.

According to X-ray analysis of the structure of mica (muscovite), 4 molecules of $KH_2Al_3(SiO_4)_3$ are contained in a unit cell of dimensions: $a = 5.17$ Å, $b = 8.96$ Å, $c = 20.05$ Å, $\beta = 84°10'$. The axes a, b, lie in the cleavage plane, and in this plane the molecules are arranged in a centered rectangular lattice which makes a pseudo-equilateral triangular network. Kikuchi was inclined to regard the "N-pattern" as a two-dimensional grating effect from the molecules in the a,b-plane, an idea with which the measured positions of the spots fully agree. It is difficult, however, to see why the scattering centers in the various parallel planes should not interfere, and Bragg[1] has given an explanation which is undoubtedly the right one. Any spot which fulfills the complete conditions for diffraction must also be a plane grating beam for any plane we choose to consider. We only have to explain why so many of the possible plane grating beams from the a,b-plane do in fact occur. Bragg considers that the mica flakes were more or less bent or warped, so that the c axis made all angles within a certain range with the direction of the incident beam at different parts of the flake. Now if this is the case, it will not require a large range of angle to insure that at least one net plane corresponding to each plane grating beam shall make the correct angle with the incident beam. The angle can be small because the ratio $c:a$ is large. Let, as before, α,β,γ be the angles a diffracted beam makes with the axes, α_0, β_0, γ_0,

[1] W. L. Bragg, *Nature*, 124, 125 (July 1929).

the corresponding angles for the incident beam. Then $a(\cos\alpha - \cos\alpha_0) = l\lambda$, $b(\cos\beta - \cos\beta_0) = m\lambda$, are the conditions for a plane grating beam from the plane of a,b, the cleavage plane. These are two of the conditions for reflection from a Bragg plane such that $Nh = l$, $Nj = m$. The third condition $c(\cos\gamma - \cos\gamma_0) = n\lambda$ remains to be satisfied. The Bragg plane with indices h,j, which makes the smallest angle with the c axis is $(hj1)$. If the range of warping of the crystal is such that in some places this makes the re-

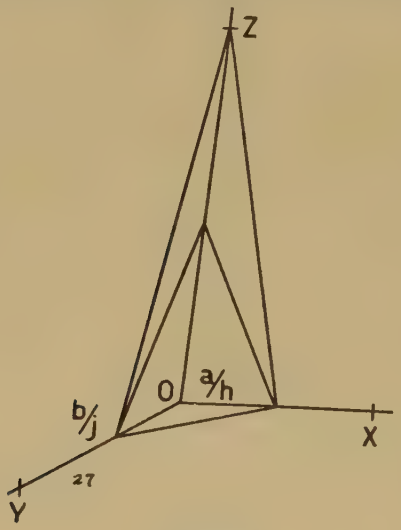
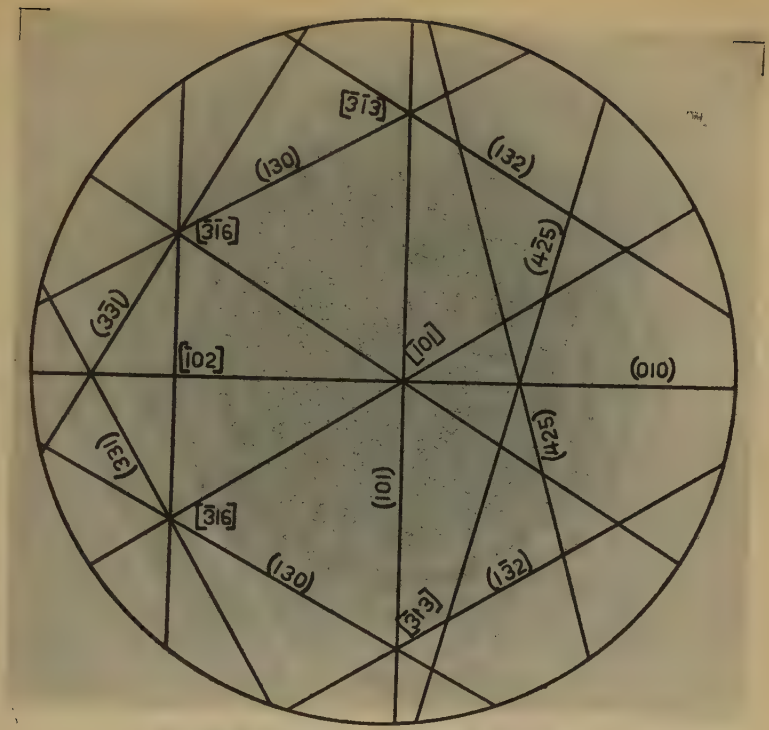


FIG. 27

quired angle with the incident ray a spot will appear. Bragg found that by turning a crystal of mica into all positions within $6\frac{1}{2}^\circ$ of a beam of X-rays he obtained a pattern of spots resembling those found by Kikuchi with electrons. The larger the number h,j, the less will be the angle between $0Z$ and the plane (Fig. 27). For large values of h,j, planes such as $(hj2)$, $(hj3)$ will make small angles with $0Z$. Further, the glancing angle required by Bragg's law is larger for these closely spaced planes; both these causes make it easier to satisfy the conditions. Whatever the value of the third index, the position of the spot, if it can exist, is determined by the plane grating conditions. As was shown on page 73, these are not appre-



a. Mica, L-pattern. $\lambda \equiv 0.0477$ Å (×1.6)

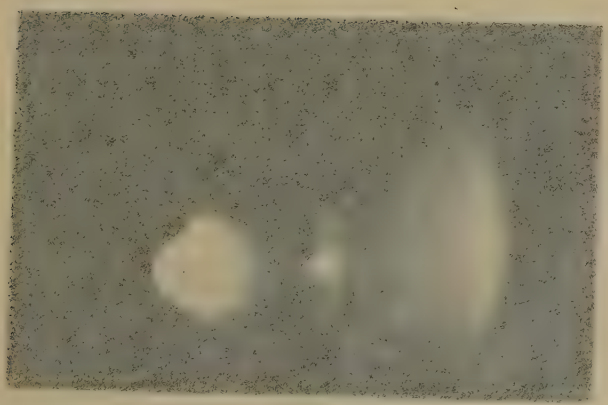
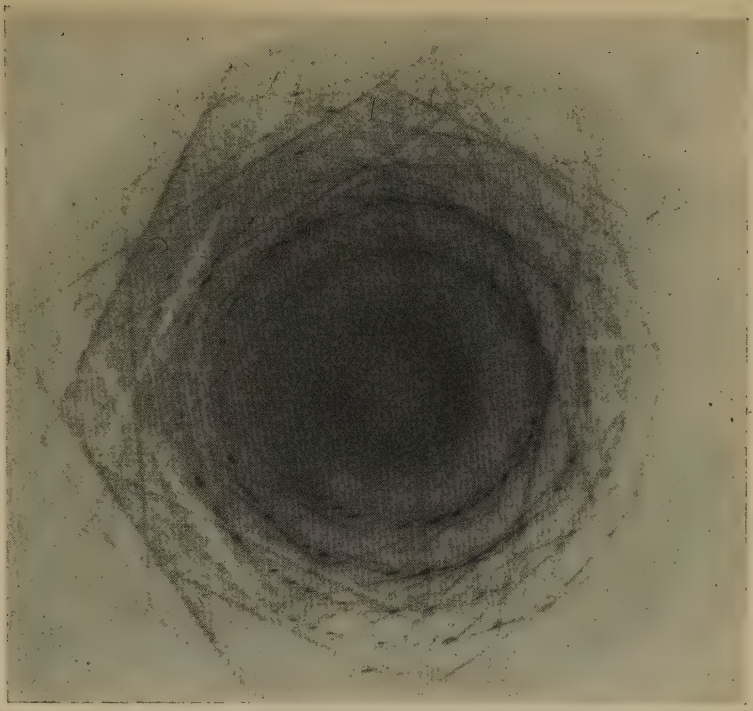
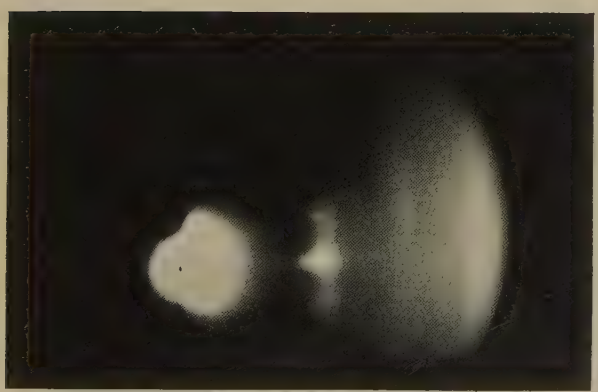


Fig. 26

a. Mica, L-pattern. $\lambda = 0.0477$Å (×1.6)



a. Mica, L-pattern. $\lambda = 0.0477$Å (×1.6)



b. Galena

FIG. 26

ciably altered by the bending of the mica so long as the angle is fairly small. Thus the spots due to a number of planes will superpose, especially at some distance from the center of the pattern, and this will tend to make the intensities constant in spite of the different reflecting powers of the different planes.

The excellent agreement with the plane-grating formula is shown in Table VI, where Kikuchi[1] has used the position of the various spots to calculate the side of the equilateral triangle, which is the axis *a*. The mean is 5.18 while the X-ray value is 5.17.

TABLE VI.

Kikuchi's Calculation of a

Current through solenoid	Energy of electron (KV)	λ (Å)	*a* (calculated) (Å)
7.20	78.0	0.0432	5.15
6.80	69.9	0.0456	5.23
6.30	60.5	0.0492	5.18
5.50	46.5	0.0563	5.21
4.80	35.7	0.0646	5.19
4.40	29.8	0.0705	5.22
4.00	24.9	0.0775	5.10
3.80	22.4	0.0816	5.15
3.50	19.1	0.0886	5.13
3.00	14.1	0.1032	5.20

The second type, or L-pattern, is simply the Laue pattern of the mica. The pieces are now thick enough not to bend much and, in theory, spots would be found with monochromatic rays only by a chance coincidence. Only those spots out of the plane grating pattern would be preserved which satisfied the third condition. This condition is equivalent to saying that the spots lie on one of a series of cones with *OZ* as axis, whose intersections with the plate give a series of ellipses. In practice any plane-grating spot which lies near an ellipse will come out strongly, owing to the various imperfections, and the pattern will become one of spots on or near ellipses.

[1] S. Kikuchi, *Japanese Journal of Physics*, **5**, 87 (1928).

A specially simple case arises when the axis of the cones is the direction of the incident rays. The axis may be any line joining two lattice points in different a,b-planes, for we can draw the unit cell in an infinite variety of ways, *e.g.* OZ, OZ_1, OZ_2 (Fig. 28), are all possible, though naturally those corresponding to simple periods will give the most strongly marked results. In this case the condition that the two successive lattice points along the incident ray shall be in phase is $c(1-\cos\phi) = n\lambda$ or $\sin\frac{1}{2}\phi = \sqrt{n\lambda/2c}$ (Fig. 29). Thus there will be a series of concentric circles whose radii are in the ratio of the square root of the wave-length. Such circles are actually found (see

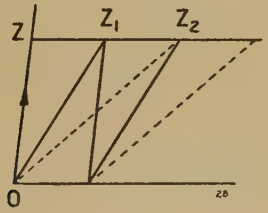


FIG. 28

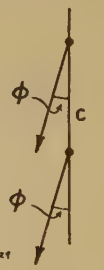


FIG. 29

Figure 25, b). If the mica is displaced slightly from such position one may have a circle (strictly an ellipse) through the central spot corresponding to $n = 0$ (Figure 26, a). A prominent feature of these patterns are the black lines passing one through each spot, and running perpendicular to the line joining the spot in question to the undeflected spot. These lines often form envelopes, and give the circles of spots the appearance of being continuous. They are accompanied by parallel white lines ("black" and "white" refer to the developed plate, or negative). Kikuchi's explanation of these is as follows. When the electron beam enters the mica there will be a certain amount of scattering, in some cases elastic. The scattered rays will be reflected from the crystal plane at the Bragg angle. For example, in Figure 30, the plane AB reflects to Q rays which otherwise would have gone to P. Conversely $A'B'$ sends rays to P and robs Q. But the scattering for large angles is presumably less than for small. Hence

Q on the whole gains and P loses, Q becomes a black line and P a white. The angle between P and Q is 2θ and the distance between white and black lines on the plate is $S = 2L\theta = \frac{LN\lambda}{d}$, where d is the spacing of the planes. If there is more than one order, N, of reflection, there will be several pairs of black and white lines. Such are in fact observed. Strictly the lines are not straight but portions of hyperbolas of small curvature. Kikuchi finds he can determine the orientation of the crystal by observation

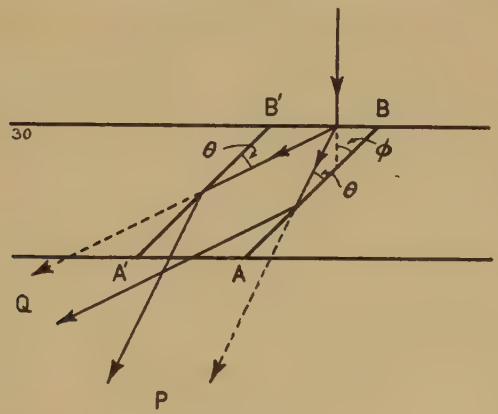


FIG. 30

of the various lines, for the intersection of various net planes with the photographic plate is midway between the light and black lines. In Figures 25, b and 26, a are shown the various intersections of these lines with the planes numbered. These intersections of the planes give the zone axes (indices in brackets). Table VII, from Kikuchi,[1] shows the values of the various spacings, d, calculated from the distance apart of the lines. In its detailed complexity this work is specially striking evidence for the truth of the wave theory.

Szczeniewski[2] has studied the reflection of electrons from a cleavage plane of bismuth. Using voltages of 62, 139 and 240, he found well-marked specular reflection, and

[1] Kikuchi, *op. cit.*, p. 94.
[2] Szczeniewski, *Compt. rend.*, 187, 106 (1928).

the angles at which the reflected beam was a maximum agreed with the simple theory to within a few per cent.

Muto and Yamaguti[1] have obtained good rings from powders of magnesium oxide and graphite deposited on spider's web. The spacings agree well with those found for X-rays, and the intensities agree fairly.

Mons. Ponte[2] has got some beautiful photographs with zinc and cadmium oxides, the patterns here also agree well with theory. Mr. Otty, working at Aberdeen, finds

TABLE VII
Kikuchi's Calculations of d.

Indices of planes	*d* in Å		Indices of planes	*d* in Å	
	Cathode rays	X-rays		Cathode rays	X-rays
(010)	9.00	8.98	(331)	1.50	1.49
(100)	5.16	5.13	(061)	1.48	1.48
(120)	3.43	3.39	(331)	1.47	1.47
(130)	2.57	2.58	(161)	1.43	1.43
(131)	2.60	2.59	(261)	1.31	1.30
(201)	2.55	2.58	(171)	1.22	1.24
(132)	2.57	2.53	(353)	1.21	1.23
(201)	2.49	2.52	(425)	1.23	1.22
(203)	2.50	2.49	(193)	0.97	0.97
(231)	1.95	1.96	(391)	0.88	0.86
(051)	1.78	1.79	—	—	—

that good photographs can be obtained with films of zinc oxide, made by dipping a loop of wire under the surface of molten zinc covered with a little chloride as flux, and slowly withdrawing the wire.

REFLECTION

Nishikawa and Kikuchi[3] have shown that even an insulator, like calcite, can be made to give diffraction patterns by reflection of electrons. The patterns took the form of black and white lines from which the spacings were calculated as above for mica. The agreement was

[1] T. Muto and T. Yamaguti, *Proc. Imp. Jap. Acad.*, **5**, 122 (1929).
[2] Ponte, *Compt. rend.* 188, 244, 909 (1929).
[3] Nishikawa and Kikuchi, *Proc. Imp. Jap. Acad.*, 4, 475 (1928); *Nature*, 121, 1019 (1928).

good. Emslie,[1] in the course of some investigations on the influence of electronic refractive index on diffraction has also observed these lines with calcite, but not with galena which is a conductor.

DIFFRACTION BY RULED GRATING

In a very interesting piece of work Rupp[2] has succeeded in demonstrating the reflection of electrons by a ruled grating, at very oblique incidence, another instance of the application of X-ray technique to electrons.

Great care was taken over the lining up of the grating and the adjustment of the beams, which was carried out optically using a photo-electric cell. The grating, which had 1300 lines per cm., was bombarded with electrons every few minutes during the experiments to remove layers of gas. The energy of the electrons to be diffracted was, in different experiments, 70, 150 and 310 volts. Besides the regularly reflected beam one, two or three orders of diffracted beams were observed at greater glancing angles than that of the reflected beam, and in one case a diffracted beam was observed at a lesser angle. As it was not possible to measure the angle of incidence with sufficient accuracy, it was necessary to eliminate it by combining observations with different wave-lengths or by taking measurements of more than one order of diffraction, using the relation $n\lambda = \frac{b}{2}\alpha(\alpha+2\theta)$ between the glancing angle of incidence θ and the angle α between the reflected and diffracted beams. The results agreed with the value of λ given by de Broglie's theory to 2 or 3 per cent, within the experimental error.

[1] Emslie, *Nature*, July, 1929.
[2] E. Rupp, *Z. Physik*, **52**, 8 (1929).

CHAPTER V

Effect of a Continuous Medium on the Waves

We have seen that for the electron waves a region of potential Φ behaves as though it had a refractive index, as against infinity, of amount:

$$\mu = \sqrt{1+\Phi/P} \qquad (1)$$

The index is greater than unity if Φ is positive, *i.e.* if the electrons are attracted into the region. On almost all theories the potential of the inside of a metal differs more or less from that in free space outside it, and it is important to consider how far the existence of this refractive index is likely to modify the conclusions deduced in the last chapter as to the diffraction of electrons by metals.

A few years ago it would have been natural to take the thermionic or photo-electric potential as a measure of Φ, but the new electron theory of Sommerfeld leads to a different conclusion. Without going into the details of this theory, we can derive the necessary formula by a method which brings out the connection with the wave mechanics.

Sommerfeld's theory of the inner potential

Consider a hollow cube of side a, and suppose it a perfect reflector for electron waves. Let us calculate the number of possible different stationary vibrations inside, which fulfill the condition of making the wave function vanish over the surfaces of the cube. Take three intersecting edges of the cube as axes. A wave progressing in a direction (lmn) has for its equation

$$\psi = \cos\frac{2\pi}{\lambda}(lx+my+nz-Vt)$$

taking the amplitude as unity for simplicity. The wave derived from this by reflection at the plane $x=0$, is

$$\cos\frac{2\pi}{\lambda}(-lx+my+nz-Vt+\gamma_1)$$

where $2\pi\gamma_1/\lambda$ is a phase angle to be determined.

The total group of waves reflected in succession from all the faces is represented by

$$\cos\frac{2\pi}{\lambda}(\pm lx\pm my\pm nz-Vt+\gamma).$$

Choose the γ's as 0 or $\lambda/2$ so as to produce the following set of eight waves:

$$\psi=\cos\frac{2\pi}{\lambda}(lx+my+nz-Vt)-\cos\frac{2\pi}{\lambda}(lx+my+nz+Vt)$$
$$-\cos\frac{2\pi}{\lambda}(-lx+my+nz-Vt)+\cos\frac{2\pi}{\lambda}(-lx+my+nz+Vt)$$
$$-\cos\frac{2\pi}{\lambda}(lx-my+nz-Vt)+\cos\frac{2\pi}{\lambda}(lx-my+nz+Vt)$$
$$-\cos\frac{2\pi}{\lambda}(lx-my-nz-Vt)+\cos\frac{2\pi}{\lambda}(lx+my-nz+Vt).$$

Combining them in pairs:

$$\psi/2\sin\frac{2\pi}{\lambda}Vt=\sin\frac{2\pi}{\lambda}(lx+my+nz)-\sin\frac{2\pi}{\lambda}(-lx+my+nz)$$
$$-\sin\frac{2\pi}{\lambda}(lx-my+nz)-\sin\frac{2\pi}{\lambda}(lx+my-nz).$$

This is zero over $x=0$, $y=0$ and $z=0$. It vanishes over $x=a$ if $0=2\sin\frac{2\pi la}{\lambda}\cos\frac{2\pi}{\lambda}(my+nz)-2\sin\frac{2\pi la}{\lambda}\cos\frac{2\pi}{\lambda}(my-nz)$, *i.e.* if $2al=n_1\lambda$ where n_1 is an integer.

Similarly the expression vanishes over $y=a$ if $2am=n_2\lambda$, and over $z=a$ if $2an=n_3\lambda$. These, then, are the conditions that the system of stationary waves is possible.

Since $l^2+m^2+n^2=1$ we have $2a/\lambda=\sqrt{n_1^2+n_2^2+n_3^2}$ and the direction cosines of the wave normals are:

$$l=\pm n_1(n_1^2+n_2^2+n_3^2)^{-\frac{1}{2}}$$
$$m=\pm n_2(n_1^2+n_2^2+n_3^2)^{-\frac{1}{2}}$$
$$n=\pm n_3(n_1^2+n_2^2+n_3^2)^{-\frac{1}{2}}$$

Each of the triplet groups of positive whole numbers, n_1,n_2,n_3, defines a set of stationary waves. Conversely, only those vibrations are possible for which the values of λ,l,m,n satisfy the above equations for integral values of n_1,n_2,n_3.

To find an approximate expression for the number of separate sets of stationary waves of this type in the cube for a given range of wave-length, consider a system of rectangular co-ordinates containing only the positive halves of the axes, and thus including one-eighth of space. Imagine in this space a simple cubic lattice of unit length. Every point of this lattice corresponds to a group n_1, n_2, n_3, of three positive integers, and so may be taken to represent a possible value of λ. The distance of the point from the origin is $r=\sqrt{n_1^2+n_2^2+n_3^2}=2a/\lambda=2az$, where z is the wave number. The number ΔZ of possible sets of stationary waves having wave numbers between z and $z+\delta z$, is equal to the number of lattice points in the octant of the sphere bounded by radii $2az$ and $2a(z+\delta z)$. Now, on an average there is one lattice point per cube. Hence $\Delta Z=\frac{1}{8}4\pi r^2 dr=4\pi a^3 z^2 \delta z=4\pi V z^2 dz$, where V is the volume of the cube. This formula, though here proved for only a cube, is true for any shape. It was originally worked out by Lord Rayleigh for light waves, and later and more accurately by Jeans.

For the electron waves $z=mu/h$ for slow speeds, therefore

$$\Delta Z=\frac{4\pi V m^3}{h^3}u^2 du \qquad (2)$$

If we construct a so-called "momentum space" such that the co-ordinates of any point in it are the components of the momentum along the axes, all the points corresponding to velocities between u and $u+\delta u$ will lie between the spheres of radii mu and $m(u+\delta u)$ inclosing a volume $4\pi m^3 u^2 du=\delta V'$. Thus $\Delta Z=V\delta V'/h^3$, and Z, the number of waves longer than λ_0, is equal to VV'/h^3 where V' is the volume of the momentum space corresponding to a momentum less than h/λ_0.

If Γ is the corresponding volume of the so-called "phase-space" of six dimensions combining the ordinary space V with the momentum space, $\Gamma=VV'$ and $Z=\Gamma/h^3$.

Now according to Pauli's principle only one electron in an atom can be associated with each set of four quantum numbers. One of these quantum numbers, corresponding to the "spin" on the orbit model, has only two possible values. Thus we can translate this into wave mechanics

by saying that each stationary vibration in an atom has, at most, two electrons associated with it. If we extend this to the present problem we can suppose that, *at most, two electrons are associated with each of the sets of waves calculated above*. In terms of the phase-space, this is equivalent to supposing that the latter is divided into cells of volume h^3, each of which can contain, at most, two electrons. The momentum space may be supposed divided into cells of volume h^3/V, such that only one value of the momentum is possible in each; this value being associated with not more than two electrons.

Thus consider, for example, a piece of metal of volume V containing N conductivity electrons, which we will suppose can be treated as in an empty space. If they all occupy the cells nearest the origin in the momentum space, the number of cells required will be N/2, the size of each is h^3/V, thus the radius p of the sphere which they will fill is given by $Nh^3/2V = \frac{4\pi}{3} p^3$. Some of the electrons, then, must have at least the momentum p. If all the cells of lower momentum are not filled, at least some of the electrons must have still larger momentum. Presumably at the absolute zero the lowest cells will be filled, the maximum momentum will be $h(3N/8\pi V)^{\frac{1}{3}}$ and the corresponding kinetic energy:

$$\tfrac{1}{2}mu^2 = \frac{h^2}{8m}(3N/\pi V)^{\frac{2}{3}} \qquad (3)$$

Thus even at absolute zero many of the electrons will have considerable energy. For even one conductivity electron per atom the energy is of the order of 6 volts. Since the energy at room temperature is about 1/30 volt this degree of heat will not make much difference in the distribution. Sommerfeld shows, by an application of the Fermi statistics, that the faster electrons show a Maxwellian distribution from a value of energy slightly less than that given above. Though this involves only a small proportion of the total number of electrons, it is important, as this variation in energy enables the usual formula for thermionic emission to be derived correctly. The work

function χ in the thermionic equation $I=AT^2e^{-\chi/kT}$ is, however, no longer the difference of potential between the inside and the outside of the metal, but is measured effectively from a level approximately corresponding to the kinetic energy of the mass of the faster electrons, given by Equation (3). Thus the true difference of potential is greater than χ by the latter quantity, in fact it is:

$$\Phi=\chi+\frac{h^2}{8\pi}(3N/\pi V)^{\frac{2}{3}} \tag{4}$$

approximately. A more accurate value given by Sommerfeld is:

$$\Phi=\chi+\frac{h^2}{8\pi}(3N/\pi V)^{\frac{2}{3}}-\frac{\pi^2}{12}\frac{8m}{h^2}(\pi V/3N)^{\frac{2}{3}}k^2T^2 \tag{5}$$

EFFECT OF REFRACTIVE INDEX ON ELECTRON DIFFRACTION

In considering the effect of a value of μ other than unity, two specially important cases arise. In Figure 31, case (a) the electrons are incident on a surface which is parallel to one of the Bragg planes and we consider reflections from this plane. If $2d\sin\theta=n\lambda$ then 2θ is the deviation which would occur in the absence of refraction. Let ϕ be the observed deviation, and θ' the glancing angle in the metal. Then, by Snell's law, $\cos\frac{1}{2}\phi=\mu\cos\theta'$ and

$2d\sin\theta'=n\lambda'=n\lambda/\mu$. Thus $\dfrac{\cos\frac{1}{2}\phi}{\mu}=\sqrt{1-\dfrac{n^2\lambda^2}{4d^2\mu^2}}$

and (by Equation 1)

$$\sin^2\tfrac{1}{2}\phi=1-\mu^2+\frac{n^2\lambda^2}{4d^2}=\frac{n^2\lambda^2}{4d^2}-\frac{\Phi}{P} \tag{6}$$

Note that $\mu^2<1+n^2\lambda^2/4d^2$ for the reflection to be a possible one. If i is the angle of incidence:

$$\mu^2=n^2\lambda^2/4d^2+\sin^2 i \tag{7}$$

a formula used by Davisson. The relative change in angle can be found from:

$$\sin^2\tfrac{1}{2}\phi/\sin^2\theta=1-\frac{4\Phi d^2}{Pn^2\lambda^2}=1-\Phi\,\frac{8emd^2}{n^2h^2} \tag{8}$$

It follows from the last result that no reflection will occur if $\Phi>n^2h^2/8emd^2$, and also that the same fractional

change in the sine of the half-deviation occurs for given n and d whatever the value of P. Thus high-speed electrons afford as good a chance of measuring Φ by observing the difference between $\frac{1}{2}\phi$ and θ, as do slow ones. Substituting for $\sin\theta$ we have:

$$\sin\tfrac{1}{2}\phi = \frac{n\lambda}{2d}\sqrt{1-\Phi\frac{8emd^2}{n^2h^2}} \qquad (9)$$

In Figure 31, cases (b) and (c) the electrons are incident normally on a parallel plate of metal containing the crystals. It is immaterial to the calculation whether the elec-

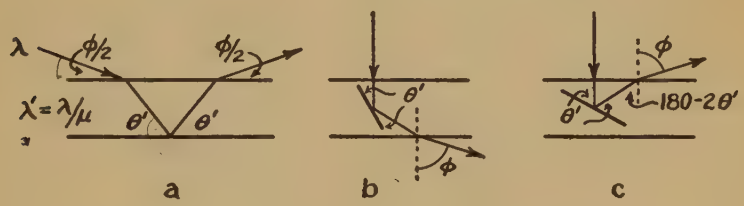


FIG. 31

trons observed are those from the same or from the opposite side of the plate as that on which the rays are incident. We have $2d\sin\theta = n\lambda$ for the angle of reflection if $\mu = 1$, and in general $2d\sin\theta' = n\lambda' = n\lambda/\mu$ and $\mu\sin 2\theta' = \sin\phi$. Hence, $\sin\phi = 2\mu\sin\theta'\cos\theta' = n\lambda/d.\cos\theta'$ which, when θ' is small, is approximately 2θ. Thus in this case the effects of refraction cancel. This, together with the small ratio of Φ/P, explains the absence of refractive effects in experiments such as those by Kikuchi or by the writer. In general:

$$\sin\phi = \frac{n\lambda}{d}\sqrt{1-\frac{n^2\lambda^2}{4d^2\mu^2}} \qquad (10)$$

and

$$\sin\phi/\sin 2\theta = \cos\theta'/\cos\theta = \sqrt{4d^2-\frac{n^2\lambda^2}{\mu^2}} \Big/ \sqrt{4d^2-n^2\lambda^2} \qquad (11)$$

If

$$\frac{n\lambda}{d}\sqrt{1-\frac{n^2\lambda^2}{4d^2\mu^2}} > 1 \qquad (12)$$

no beam will appear.

Experimental evidence

We have seen on page 54 that Davisson's and Germer's results do not agree entirely with the simple theory. It was suggested by Bethe[1] and also by Eckart[2] that the explanation lay in the neglect of the refractive index. At first a correlation between observed and theoretical beams was assumed which gave $\mu < 1$; later, with another correlation, Bethe found good agreement for these early experiments with $\mu > 1$ and corresponding to a value for Φ of 15 volts. It appears from the later work that this was, in part, a

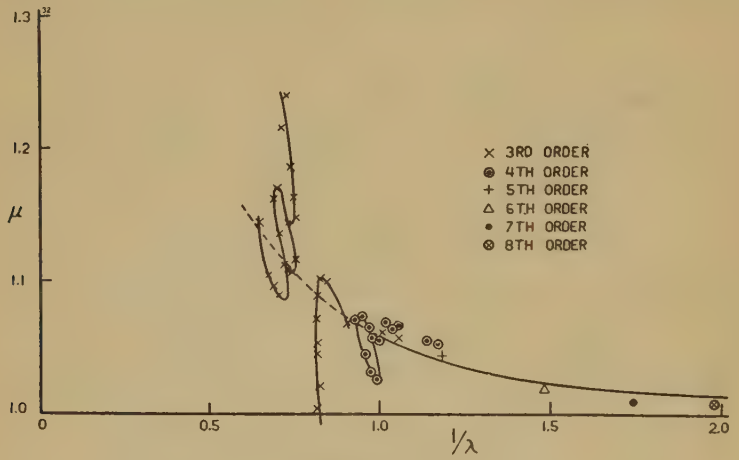


FIG. 32

fortunate coincidence. Some of the beams which would have been expected from the X-ray analogy are not observed, owing to relation (12) above not being satisfied.

Davisson and Germer[3] studied the question in detail using the "reflection" apparatus described on page 53. Figure 15 on page 53 shows the intensity of the regular reflection as a function of the wave-length. The reflection was in the *A* azimuth. The vertical lines represent the position of the calculated maxima ignoring refraction. It will be noticed that the higher orders nearly agree with the experiments; these are the waves corresponding to

[1] Bethe, *Naturwissenschaften*, **15**, 787 (1927); *ibid.*, **16**, 333 (1928).
[2] Eckart, *Proc. Nat. Acad. Sci.*, **13**, 460 (1927).
[3] Davisson and Germer, *Proc. Nat. Acad. Sci.*, **14**, 619 (1928).

the fast electrons for which μ is probably nearly unity. Making the assumption that these maxima do in fact correspond, we can calculate the refractive index required to make the others fit. It is greater than unity in all cases. It will be noticed that there are subsidiary maxima which agree well with the simple theory at the third and fourth orders. Davisson considers that these may represent the constructive interference of waves from the top layers of adjacent portions of crystal at different levels. The phase difference between waves reflected from such steps would

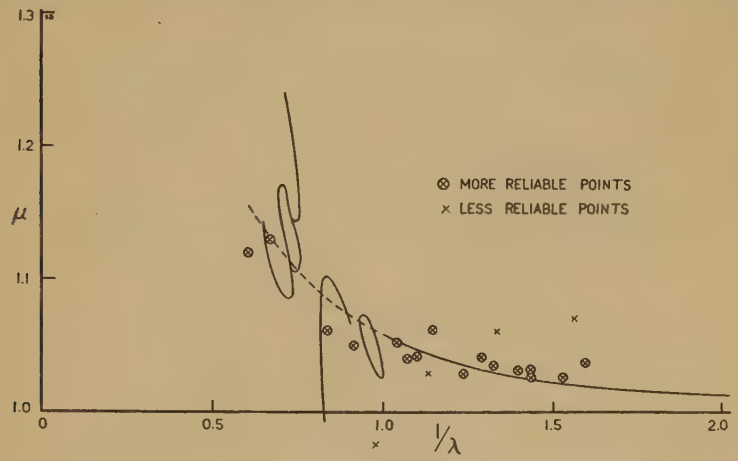


FIG. 33

be accurately given by the simple law since the path difference occurs in vacuo.

Davisson and Germer find the best fit with $\Phi = 18$ volts. The value of the refractive index calculated from the new experiments is shown in Figure 32, and also that from the older experiments in Figure 33. The smooth curve is that given by $\mu = \sqrt{1 + 18/P}$. It will be seen that while the agreement is fair at the shorter wave-lengths, there is a complete failure for λ greater than 1.00Å. In appearance the points faintly recall the appearance of a curve of anomalous dispersion, but there is no known theoretical reason for such an effect, nor does the voltage—about 90—of the middle of the region correspond to any known critical potential of nickel. A probable explanation is considered on page 103.

Rupp's Experiments. In his first paper Rupp calculated values of the refractive index for the electrons by a formula which was equivalent to neglecting the bending of the rays on emergence. Though the experiments lead to reasonable values of Φ for the metals used, there seems no theoretical justification for the method of calculation. If the films consisted of irregular lumps instead of being plane-parallel, the chief effect of the refractive index would probably be a broadening of the rings without marked change in size. A detailed calculation of the effect of an inclined film

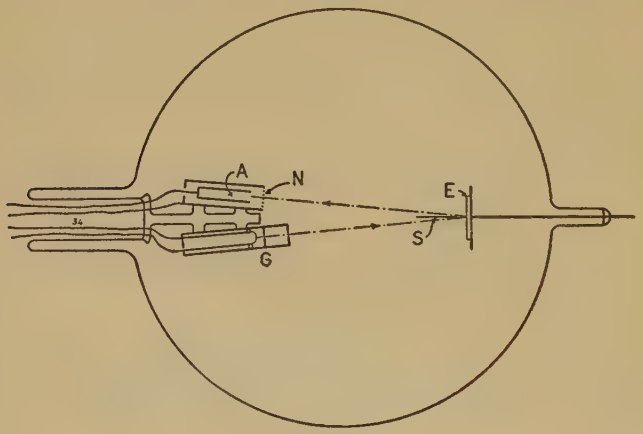


FIG. 34

shows there is a shift of the center of $\overline{\mu-1}\,L \tan i \tan^2 2\theta$ where i is the angle of incidence to the film and θ the glancing angle in the crystal. In addition, the circle becomes an ellipse whose minor axis is increased in the ratio $\cos\theta' : \cos\theta$ (see p. 95), while the ratio of the axes is $1+\overline{\mu-1}\,\dfrac{\tan^2 i}{\cos^2 2\theta}$. Thus, for a film which could be regarded as composed of a large number of flat pieces inclined at random, the rings would be broadened owing to the varying shifts of the centers, and slightly increased in size.[1] The latter effect is in the opposite direction to that given by Rupp's calculation.

[1] Rupp—*Ann. Physik*, (5)1, 773 (1929)—attempts to investigate the effect of refractive index by inclining the film. He found only a broadening. The shift, calculated in §14 of his paper as 40 per cent, is the result of a numerical error. The true value is 6 per cent of the radius or 3 per cent of the diameter.

Some later reflection experiments are not subject to these objections.[1] The apparatus, shown in Figure 34, is similar in principle to that used by Davisson and Germer in their later work, but the angles of incidence and reflection were kept fixed at 10°. The target, consisting of a thin film which had been partially turned into a single crystal by heating, is shown at *E*, *G* is the electron gun and *A* the Faraday cylinder. Electrons which had lost much energy were turned back by a potential applied to the net *N*. The razor blade *S*, perpendicular to the surface of the target and nearly touching it, serves to limit the beam of electrons actually used. Figure 35 shows the relation between the current to the Faraday cylinder and the voltage of the rays in one set of experiments. The position

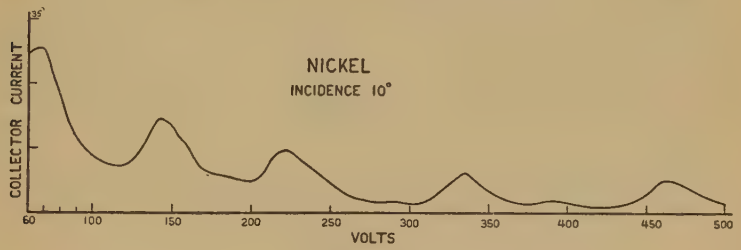


FIG. 35

of the maxima give the wave-lengths of Bragg reflection from which μ can be calculated by Equation (6). The values found for Φ showed no systematic change with voltage. The mean values were: Nickel 16, Copper 14, Silver 14, Gold 14, Aluminum 17, Lead 11. The value for lead is less accurate than the others. It was found not necessary to assume any anomalous dispersion or variation of Φ. The values found for Φ ranged over 2 or 3 volts on either side of the mean.

An examination of these results on the lines of the Sommerfeld theory[2] shows that they are consistent with Equation (4) within the rather wide range of uncertainty of χ, the thermionic work function, if from 2 to 4 conductivity electrons are assumed per atom. There is, however, no

[1] Rupp, *Ann. Physik*, (5) 1, 801 (1929).

[2] See Rosenfeld and Witmer—*Z. Physik*, 49, 534 (1928)—who, however, use Rupp's earlier and incorrect values of Φ.

certainty that this number is integral. Incidentally it may be remarked that, owing to the relation between Φ and χ, anything which alters the work function of a metal surface must also affect electronic diffraction from it.

A series of experiments by Rose[1] with an aluminum crystal are noteworthy in that they show no sign of a refractive index. The electrons, of 50–250 volts, were incident on the crystal at a variable angle, and the position of the collector, a Faraday cylinder, could also be varied. The

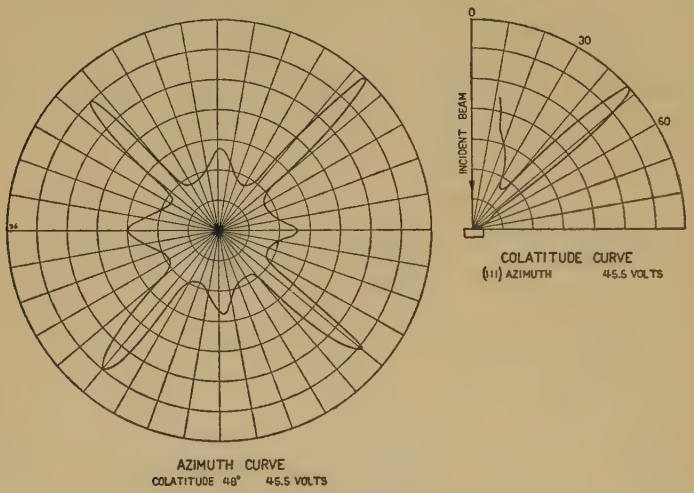


FIG. 36

voltage was kept constant during a run and the position found for the sharpest reflected beam. This always occurred with the angle of incidence equal to that of reflection, but the angle depended, of course, on the voltage. Four different orders were found which agreed well with theory, and two others which did not, possibly due to an oxide film. While these experiments were not so accurate as those by Davisson and Germer, the existence of a refractive index of the magnitude indicated by Rupp's experiments on aluminum should have been detectable. It is conceivable that the state of the crystal surface may have a marked influence.

[1] Rose, *Phil. Mag.*, (7) 6, 712 (1928).

Farnsworth[1] has examined the diffraction of electrons by the (100) face of a single copper crystal at normal incidence. The beams obtained were very sharp, as shown by the specimen illustrated in Figure 36. Most of the beams to be expected theoretically were obtained, and showed a tolerable agreement when plotted on a λ-sinϕ basis. The beams came at voltages varying from 11 to 236. So far the results resemble those of Davisson and Germer, but Farnsworth also found "additional" beams exceeding in number the regular ones; many of these additional beams were very strong and sharp, indeed the one illustrated belongs to this group. When plotted on a λ-sinϕ basis many of these beams lie somewhere near the lines which correspond to half-orders, or what is equivalent to a doubled spacing of the surface layers. Davisson and Germer have obtained a similar result due to gas films, but Farnsworth rejects this explanation on the ground that the beams in question are "space" beams, *i.e.* sharp in voltage, and that they do not vary in intensity with heat treatment in the way beams due to a gas film should. I have found that the thin film of oxide which forms on the surface of copper in air gives quite good diffraction patterns by reflection, even with electrons of the energy of 30,000 volts. With slow electrons the effect of quite imperceptible layers might be enough to account for the effects observed, though it is rather surprising that the crystals of cuprous oxide should follow the azimuth of the original copper crystal as closely as Farnsworth's results would imply. There is also the possibility that these results are to be classed with those of Rupp and Tartakovsky and indicate a possibility of reflection from "forbidden" crystal planes, *e.g.* (100) in a face-centered cube. There seems, at present, no theoretical explanation possible for such an occurrence.

Farnsworth tabulates the values of Φ required to make the beams coincide with the nearest theoretical beams (half-orders allowed). He calculates Φ by subtracting the actual voltage of the electrons from the voltage V given by $V = 150/\lambda^2$, where λ is the wave-length in Ångström units which would give a spot in the observed position, ignoring

[1] Farnsworth, *Phys. Rev.*, 34, 677 (1929).

refraction. This process is equivalent to ignoring the bending of the waves on emerging from the crystal. It does not seem as if his results can be explained by the assumption of any probable refractive index of the ordinary kind. It is very desirable that the results should be examined in the light of the more complete theory discussed on pages 103-107.

Miss Davis[1] mentions experiments on cobalt which appear to indicate a Φ of 4–5 volts, but it is not clear from her short account that the deduction is justified.

We have seen that with arrangement Figure 31 (a) the refractive index may produce a large relative shift in the diffracted beams even with fast electrons. Emslie has used this fact to apply the technique of cathode rays and photographic detection in investigating the refractive index of certain crystals for electrons. A beam of cathode rays passes through a fine tube and strikes the face of the crystal at a small adjustable angle. The diffracted beams are received on a photographic plate held in a camera of the same type as that used by the author. Strong spots were obtained on the photographic plate by diffraction from the cleavage faces of galena (100), antimony (111) and calcite(100). For each spot $\sqrt{P}\sin\phi$ was constant, a result which is easily seen to be in agreement with Equation (9). The voltages used were 10,000 to 45,000. In the case of galena there was one bright spot on the equator and two other spots vertically above and below it, while farther out were two fainter vertical lines Figure 26(b) (the portion of a circle to the right is where the scattered electrons are cut off by the camera). By choosing $\Phi = 18.2$ volts Equation (9) was satisfied for the bright spot and vertical lines with $n = 6$, 8, and 10. With this value of Φ the lower orders would be extinguished. The side spots could be explained by supposing that the crystal surface was rough and that the exposed surface was the reflecting plane (602). They did not fit any possible plane if the refraction took place at the (100) plane. The pattern for antimony was similar, but less well marked. The best fit gave $\Phi = 25$ volts. The case of calcite was interesting owing to its being an insulator. There was occasionally some charging up, but not

[1] M. Davis, *Nature*, **123**, 680 (May 24, 1929).

much, the balance being probably maintained by the emission of δ-rays. There were two spots on the equator line which corresponded to the 3d and 4th orders of reflection from the cleavage plane for $\Phi = 22$ volts. For this value the 1st and 2d orders would be extinguished. Some intersecting lines, similar to those found by Kikuchi, were also observed.

In some unpublished experiments the present writer has observed that the spots with galena show a marked fatigue effect, but recover on standing over night. They also show a gradual change from day to day, corresponding

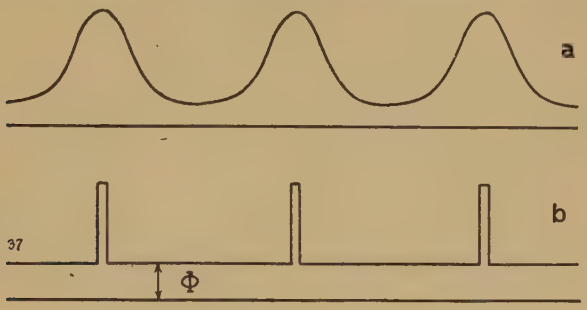


FIG. 37

to a change in Φ from about 9 volts to the value of 18 volts found by Emslie. These changes appear to be connected with changes produced in the crystal by the cathode rays, for the surface of the crystal shows marked discoloration after prolonged use. In these experiments it is necessary to rotate the crystal to make the different spots appear at their brightest on the willemite screen but, owing probably to the imperfect flatness of the crystal, a setting can often be found where several appear fairly brightly.

GENERAL THEORY OF CRYSTAL DIFFRACTION

In the investigations made so far we have taken account of the influence of the material of the crystal on the scattering of the electrons in two quite separate ways. Firstly, we regarded the material as composed of scattering points, and secondly we regarded it as causing a field of constant potential Φ. Now these are idealizations in opposite directions of the same reality, the actual field of

the atoms; in the one case we accentuate the individuality of the atoms, in the other we merge it into a constant field. The combination of the two views will give a better approximation to the truth than either separately, as indeed we have found above, but it is still far from the truth. In effect we are representing a distribution of potential which is really something like Figure 37 (a), by the approximate distribution illustrated at (b). To progress further we need to consider generally the interaction of a wave system

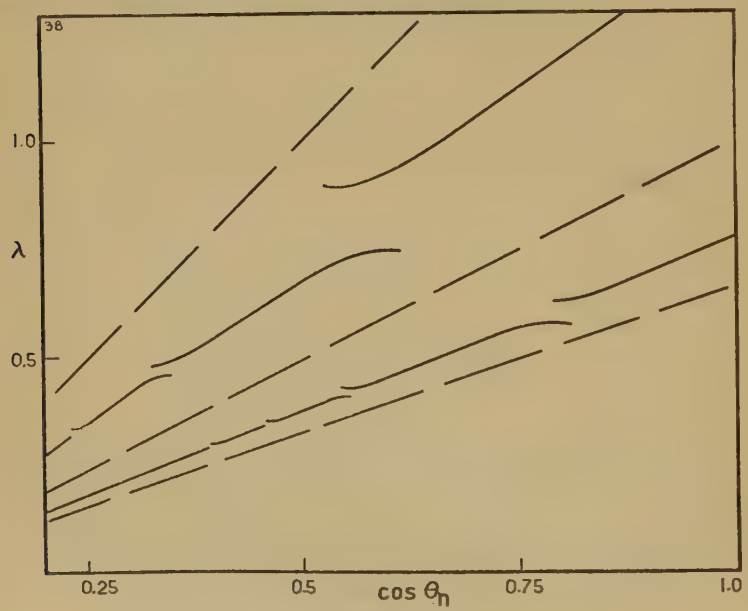


FIG. 38

with a field of potential of the most general form which is periodic in three directions, in other words, a field expressed by a three-dimensional Fourier series.

Dr. P. M. Morse of Princeton has made considerable progress with this problem and through his kindness I am enabled to indicate some of the results of his work which is shortly to appear in the *Physical Review*.[1] Morse considers the propagation of waves satisfying Equation (5), p. 29, through a medium in which the potential V is given by an expression of the form:

[1] P. M. Morse, *Phys. Rev.*, **35**, 1310-24 (June 1, 1930).

$$\sum_l A_{xl} e^{il\alpha x} + \sum_m A_{ym} e^{im\beta y} + \sum_n A_{zn} e^{in\gamma z}$$

where α,β,γ, are equal to 2π divided by the corresponding lattice spacings. Though not the most general triply periodic expression, this is general enough for most purposes. He finds, as might be expected, that there are certain directions in the crystal in which the waves are highly damped. These are the directions corresponding to the Bragg reflections from various crystal planes. Treating

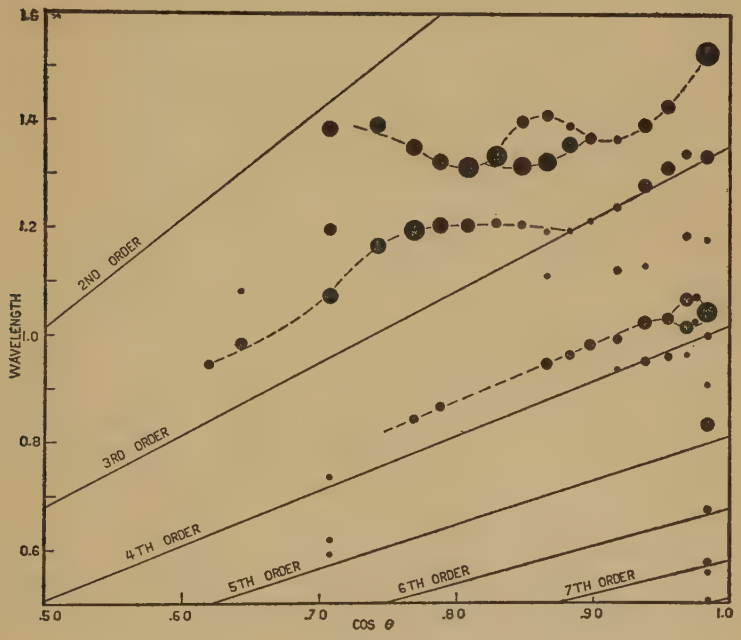


FIG. 39

The positions of the dots on this figure correlate the wave-lengths and the angle of incidence at which electron reflection occurs from a (111) face of a nickel crystal The area of each dot represents the intensity of the reflection.

first a one-dimensional case of normal incidence at a crystal surface, he shows that the maximum of reflection will occur near but not quite at the wave-length given by the Bragg law, assuming a refractive index of $\sqrt{1+\Phi/P}$ where Φ is the average value of V. The difference depends on the exact form assumed for the variation of V near the surface.

The case of oblique incidence is more complicated, and only the two-dimensional problem is solved. The method consists of equating values of ψ and $\frac{\partial\psi}{\partial x}$ on both sides of the surface of separation as in classical wave problems. The conclusion is that the behavior of the crystal closely approximates to that of the simple theory except in certain special cases when $\frac{2\pi}{\lambda}\sin\theta$ is near $\frac{m\beta}{2}$, where λ is the wavelength in free space, θ is the angle between the incident beam and the normal, m is an integer, and β corresponds to the spacing in a direction parallel to the crystal surface. This condition is equivalent to $m\lambda \backsimeq 2b\sin\theta$, where b is the length of the axis *in* the crystal surface. If this relation happens to be compatible with the Bragg expression—which may be written in this notation, $\cos^2\theta_n = \frac{n^2\lambda^2}{4d^2} - \frac{\Phi}{P}$ — the reflection will not obey the Bragg law, but will occur under conditions more or less seriously modified. On the ordinary theory if λ is plotted against $\cos\theta_n$, the angle of maximum regular reflection (on our original notation $=\sin\theta$), the points according to the Bragg analysis should be on straight lines through the origin. In Figure 38 the dotted lines are the Bragg lines for an index of refraction equal to unity. The full lines are those calculated on a certain assumed distribution of potential and their broken nature is certainly strongly reminiscent of the general distribution of the beams in Davisson's and Germer's experiments, which are shown plotted in the same way in Figure 39. There seems to be tolerable agreement with the places near where the breaks occur, but the form of the calculated curve is sensitive to the precise assumption made as to the form of the potential function.

Sir J. J. Thomson, in a recent article,[1] has examined the same problem. His work is based on the electrodynamic theory discussed in Chapter VIII, but the equation which serves as a starting point for the discussion of the diffraction by crystals is practically Equation (5), p. 29, so that

[1] J. J. Thomson, *Phil. Mag.*, (7) 8, 1073 (1929).

the conclusions do not depend on the particular physical assumptions used. He finds, with wave-length and angle of incidence in a certain relation, that there is a strong reflected wave and extinction of the primary. Retaining only terms to the first order in the potential of the crystal, the relation is that of Bragg's law. For higher orders of approximation there is a refractive index for the medium, but one which depends on the wave-length and angle of incidence. In fact $\mu^2 = \cos^2 i + \frac{\lambda^2}{4b^2}[1 + \sqrt{(\theta_0 - 1)^2 - \theta_1^2}]$ where i is the incident glancing angle, λ is the wave-length outside the crystal, b the spacing of the planes of the crystal which are parallel to the free surface, $\theta_0 = \frac{4b^2}{\lambda^2}\sin^2 i$, and θ_1 measures the amplitude of the periodic variation in potential—assumed simple harmonic—in the crystal. If the maximum potential is V volts, $\theta_1 = V/80$ approximately. The condition for a strong reflection is found by eliminating c between $c - 2 = -\sqrt{\theta_0}$ and $c^2 = 1 + \sqrt{(\theta_0 - 1)^2 - \theta_1^2}$ when the value of θ_0 will determine the condition. In this analysis the variation of potential along the surface was not considered, so the conclusions cannot be directly compared with those of Morse.

CHAPTER VI

Interaction Between Electrons and Atoms

All the experiments agree in concluding that the diffracted electrons are, at least for the most part, of the same energy as the original beam. This is, on the whole, to be expected because the inelastic type of interaction between atoms and electrons, such as results in the production of characteristic radiation, is essentially an action with a single atom, not with the whole crystal. Theoretically, it would be possible to observe the part of the crystal from which the characteristic radiation came, and this is inconsistent with the idea of an action between the electron and the crystal as a whole, inherent in the explanation of electron diffraction considered in the previous chapters. In addition, the diffraction, if it occurred, would presumably be that appropriate to the changed wave-length, and if the change in energy were large enough to notice that in wave-length would cause the electron to be diffracted clear of the ring due to the unchanged waves. There is, of course, nothing to prevent an electron being scattered first inelastically and then elastically; but in this case the change in direction due to the first scattering will deflect the whole diffracted pattern to an extent and in a direction which will be different in every case; this will usually cause a diffuse blackening. Kikuchi's black and white lines are instances of patterns formed by double scattering but here, apparently, both scatterings are elastic or nearly so, for otherwise the assumption that the wave-length causing the pattern is that of the original electrons would break down and one would not expect the excellent agreement with it that is actually found. Apparently, then, we must consider the possibility of a diffuse elastic as well as the diffuse inelastic scattering and also that causing the diffraction pattern.

An interesting question arises in connection with the emission of "white" X-rays. Is an electron which has lost energy in the form of radiation of this kind, scattered into a diffraction pattern? Here there is no necessary association of the radiation with one atom. If it comes from anywhere in particular it presumably comes from the moving electron. It is difficult to invent an experiment to test this point, because unless we know how much energy the electron has lost one cannot tell what wave-length it ought to have and hence whither it should be deflected. Theoretically, however, it should be possible to take a very feeble stream of electrons incident on a crystal, detect the X-rays in a Geiger counter—taking precautions to filter out any characteristic radiation—and observe the coincidences which presumably would occur between a quantum of X-rays and the arrival of an electron on a screen. It would then be necessary to observe in each case the magnitude of the quantum of the X-rays, which is theoretically possible, calculate the wave-length of the electron after producing it, and then see if the place where the electron actually arrived was near one of the diffraction spots corresponding to this wave-length in more cases than would be expected by mere chance.

The relative number of elastic and inelastic collisions is an important factor in determining the visibility of the rings. In my experiments I have found that with metals the rings always become invisible at voltages below 10,000 and often at larger voltages. Thus, for gold the limit is about 12,000, for silver 14,000, lead 15,500 and for iron 16,000. The thickness of the films was of the order 10^{-6}, as measured by their optical density. At this voltage the central spot can still be clearly seen, but the rings vanish into the diffuse background. Two or three thousand volts lower the central spot also vanishes, if the film is free from holes, but the films continue to transmit diffusely scattered electrons down to 2,000 volts for gold and aluminum. The impression one gets from studying the plates is that the rings have been swamped by the diffuse background. This could be caused by an increase in the proportion of inelastic to elastic scattering or by a general

increase in scattering of both kinds or, of course, by a combination of the two effects. If it is due to the second cause it should be curable by reducing the thickness of the film. This does, in fact, do some good but not much. Thus, a silver film of optical density 0.334 gave rings down to 14,000, while one of 1.105 density (three times as thick) was effective at 20,000 volts. Again, a lead film of density 0.105 gave rings down to 15,500 volts, while one of 0.972 had a limit of only 27,000 though 9 times as thick. Thus it would seem that the scattering must increase very rapidly as the voltage decreases, if the effects are to be explained by this cause. There seem to be no independent measures of electron scattering in this range of voltage. It is, of course, possible that the films are of uneven thickness, though they appear uniform to the eye and under the microscope; in this case the mean thickness, as measured optically, may not be much of a guide to their behavior.

Rupp's work[1] shows that in favorable circumstances diffraction rings can be produced from thin films with electrons of 150–300 volts energy, though he mentions that the films are very erratic in their behavior as regards transparency. The explanation is still uncertain. In a recent paper[2] he finds selective reflection and absorption for thin films in the region between 5 and 40 volts.

DETERMINATION OF "E" CURVE

The diffraction experiments enable one to obtain information as to the relative scattering, in different directions, of the electrons by individual atoms. The process is analogous to that by which the X-ray "F" curves can be deduced.

The intensity of each of the rings will depend on a number of factors. The corresponding case for X-rays has been thoroughly investigated, and it has been found that the total radiation in a cone of semi-apex angle 2θ, *i.e.* for planes at a glancing angle θ, is given by

$$R = kF^2\lambda^3 \frac{1+\cos^2 2\theta}{2\sin 2\theta} \cos\theta \frac{pV}{2}$$

[1] Rupp, *Ann. Physik*, 85, 981 (1928).
[2] Rupp, *Z. Physik*, 58, 145 (1929).

where V is the volume of the crystal, p is the number of planes giving the reflection and is obtained by permuting the crystal indices and their signs, λ the wave-length, k a factor corresponding to the X-ray scattering of a single electron, and F a factor which represents the number of electrons to which each atom is equivalent in scattering power. F varies with θ because the scattered waves due to the several electrons will not be exactly in phase except when $\theta = 0$, and at other angles will interfere so that the combined amplitude is less than the sum of the separate amplitudes of the several electrons. When θ is small, as in the present experiments, we may write for the linear density, D, of scattered electrons on any ring $D = k'E^2p/\theta^2$, where k' is a constant for any single photograph and E is the factor for electrons corresponding to F for X-rays. Since p is an easily calculable integer, a measurement of D for various rings will enable us to compare the values of E for the angles θ to which the different rings correspond.

The necessary measurements and calculations have been made for diffraction patterns taken with two gold films. The experimental details are as follows. Two exposures were made on each plate with the times of exposure in a known ratio, in some cases 2 : 1 in others 3 : 1. In order to make the measurements of the times sufficiently accurate, the intensity of the rays was reduced by a small magnet held near the fine tube till they gave suitable blackening with the shorter exposure 60 seconds in duration. Great care was taken to insure that the discharge was running steadily, and the pressure was kept constant by balancing the pump against an artificial leak. Plates were rejected for which there was any reason to suppose a change of conditions or on which the blackening did not lie within the range most suitable for photometric measurement. Four plates were selected for measurement, three made with one gold film and one with another. The first film was selected as giving specially good rings, the other was an average one.

The plates were developed in a Dobson tank to insure equal development all over. The density was then measured with a Lindemann photometer made by the Cambridge

Instrument Company. The measurements were made along corresponding radii of the two exposures of each plate and readings taken at 0.25 mm. intervals. The method of reduction was as follows. The densities (wedge readings) of a number of pairs of corresponding points of the two

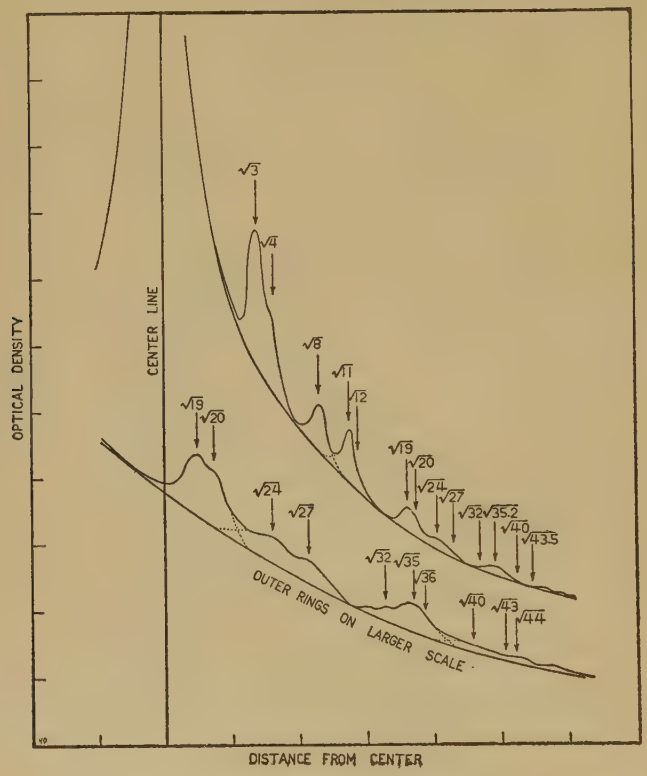


FIG. 40

exposures were tabulated. From these a curve, showing the relation between density and log It for the particular plate and the particular rays, can be constructed as follows: Each pair of densities is plotted with density as ordinate, and a difference in abscissa equal to log 2 or log 3, depending on the exposure ratio. Each pair of points is shifted parallel to the x axis until the whole lie on a smooth curve, which is the curve required. From this a second curve is drawn giving density against It, which in most cases was not far

from a straight line through the origin. The second curve can be used to transform the measured densities into numbers of particles per unit area at any part of the plate.

In practice, owing to the large number of individual readings of density, the readings themselves were not transformed, but curves were drawn of the density along the radius, of which one is shown in Figure 40. The "background" of diffuse scattering is sketched in as shown by the smooth curve, and the area under each peak measured. This area was then reduced to (relative) number of particles by multiplying by the slope of the curve connecting density with intensity, taken at a density corresponding to the center of gravity of the area of the peak. This method, which was a great saving in labor, is justified by the relatively slight curvature of the density-intensity curve.

It will be seen that the above method makes no assumptions as to the characteristics of the plate, the calculations for a plate depending only on measurements made on that particular plate. It is, indeed, assumed that the blackening depends on It, the product of intensity and time; but Ellis has shown that this law holds for the blackening produced by electrons, though it is well known to be not accurately true for that caused by light.

In many cases two or more rings were so close together that they were either not resolved at all or, if resolved, overlapped to such an extent that the intensities corresponding to them could not be determined separately with any degree of accuracy. In such cases they were treated as one ring with a mean value of θ. Table VIII shows the relative values of D thus obtained, that for the (220) ($\sqrt{8}$) ring being taken as 100 throughout. It will be seen that the four plates are in fair agreement and that the one at the higher voltage shows no appreciable difference from the others. Since the sizes of the rings vary with the wave-length of the electrons, and hence with the voltage, E must vary with λ as well as θ. For X-rays it is a function of $\sin \theta/\lambda$ and is thus the same for any ring whatever the wave-length. Within the limits of experimental accuracy the same holds here.

The mean values of D have been used to calculate the relative values of $E^2 = \theta^2 D/k'p$, the values of θ^2 being proportional to the squares of the ring radii, *i.e.* to $h^2+j^2+k^2$. In the case of the compound rings the weighted mean was used for this quantity, which is given in Table VIII.

TABLE VIII.

D in arbitrary units.

Ring $h^2+j^2+k^2$	p		April 12 P=30500 Film 59.	April 19 P=30000 Film 59.	April 22 P=29000 Film 80.	April 29 P=49300 Film 59.	Mean D	Mean $h^2+j^2+k^2$	$E^2=\frac{(h^2+j^2+k^2)D}{p}$
3	8	14	467	525	534	537	518	3.4	126
4	6								
8	12		*100*	*100*	*100*	*100*	*100*	8	67
11	24	32	110	112	143	114	120	11.25	42.2
12	8								
16	6		—	—	(12)	—	—	16	(32)
19	24	48	54.2	55.2	52.2	43.5	51.3	19.5	20.8
20	24								
24	24	56	24.1	28.6	18	18.4	22.3	25.7	10.2
27	32								
32	12	90	17.1	20.6	20	16.6	18.6	35.0	7.2
35	48								
36	30								
40	24	72	7.1	6.7	—	5.3	6.4	42.3	3.8
43	24								
44	24								
48	8	192	12.0	—	—	8.0	10.0	54.6	2.8
49	6								
51	24								
52	24								
56	48								
59	72								

Film 59 had an optical density of 0.218, probable thickness 70Å.
Film 80 had an optical density of 0.343, probable thickness 120Å.

The value of F^2 is shown in Figure 41 plotted against $\sqrt{h^2+j^2+k^2}$, *i.e.* $2a \sin\theta/\lambda$. It will be seen that it shows a rapid fall with increasing values of $\sin\theta/\lambda$, as is well known to occur for X-rays. This fall is to be expected on general considerations of interference. The closest distance

of two atoms in a face-centered cube is $a/\sqrt{2}$, which is presumably the atomic diameter. For electrons diffracted through an angle 2θ, the path difference corresponding to scattering matter at the ends of a diameter is $a \sin 2\theta/\sqrt{2} = \sqrt{2}\, a \sin\theta$, since θ is small. It thus equals $\lambda\sqrt{h^2+j^2+k^2}/\sqrt{2}$. The effect of interference in reducing the intensity would become marked if this was about $\lambda/2$, *i.e.* for a smaller

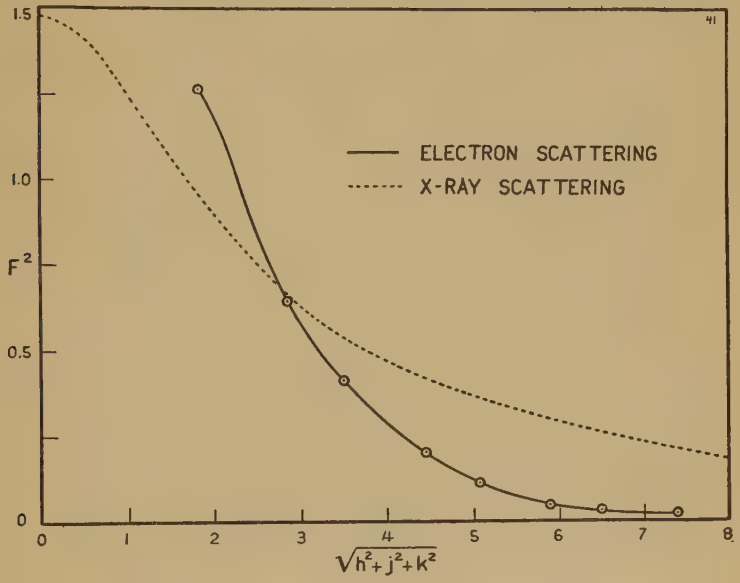


FIG. 41

value of $h^2+j^2+k^2$ than is available, so interference will be serious even for the (111) ring. If the scattering is due to the electrons which are distributed throughout the volume of the atom, the effect of interference will become more and more serious as the angle of diffraction increases, and this is what our curve shows.

Now the scattering of an electron wave by a single atom has been investigated by Born[1] and others. Taking a monochromatic plane wave as representing the incident electrons, it is found that in general the atom becomes the center of a wavelet of the same wave-length as the

[1] M. Born, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 146 (1926); *Z. Physik*, 38, 803 (1926).

original beam, and of other wavelets of longer wave-lengths. These latter correspond to inelastic collisions. These results are arrived at by finding a solution of Equation (5) p. 29, the value of F being chosen so as to fit the field of the atom. This field is regarded as producing a "perturbation" on the original wave and the method is one of successive approximations, though only the first approximation has actually been calculated except when the "atom" is a simple nucleus attracting according to the Coulomb law. In this last case the distribution of the intensity in the scattered wave is identical with the distribution of the electrons as calculated by Newtonian dynamics.

Born's approximate expression has been put into a different form by Mott.[1] If a beam of electrons passes through a gas containing n atoms per unit volume, then he defines nI_ϕ as the proportion of the beam scattered in the direction Φ per unit solid angle and per unit length of the beam. On the wave theory $I_\phi = |f(\phi)|^2$ where $f(\phi)$ is the amplitude of the scattered wave, for we suppose that the density of electrons in the scattered beam is proportional to the intensity of the waves in the corresponding direction, *i.e.* to the square of their amplitude. Mott modifies Born's expression for $f(\phi)$ into the form

$$f(\phi) = -\frac{8\pi^2 me}{h^2\mu^2}\int_0^\infty \left(1 - \frac{\sin\mu r}{\mu r}\right)\sigma dr \text{ where } \mu = \frac{4\pi}{\lambda}\sin\tfrac{1}{2}\phi$$

the atom being assumed to have spherical asymmetry and σdr being the total electronic charge between radii r and $r + dr$. This charge is assumed continuously distributed so that the potential due to it is F, and so that in the undisturbed atom the density of charge is proportional to $\psi\psi^*$.

The first term in the integral gives $\frac{Ne^2}{2mu^2\sin^2\frac{1}{2}\phi}$ since $\int_0^\infty \sigma dr = Ne$ the nuclear charge and $\lambda = h/mu$. Now this is precisely the scattering (in amplitude) of the bare nucleus,[2] which is the same both classically and wave-mechanically, if we interpret the square root of the intensity of the classical beam as being an amplitude.

[1] Mott, *Proc. Cambridge Phil. Soc.*, **25**, 306 (1929).
[2] Cf. Rutherford's $\operatorname{cosec}^4\frac{1}{2}\phi$ law for α particles.

The second term can be interpreted as follows: $\frac{\sin\mu r}{\mu r}$ can be shown[1] to be the factor by which the amplitude of a wave, scattered coherently by matter distributed over a spherical shell of radius r, is reduced by the mutual interference of the waves. The phase of the scattered wave from such a shell corresponds to that from a point at the center. If then we suppose that every element of charge $\rho dxdydz$ scatters like a fixed charge, and that the waves from the different charges interfere on account of their different lengths of path, the resulting amplitude from the charge in the region r to $r+dr$ will be $\frac{e\sigma dr}{2mu^2\sin^2\frac{1}{2}\phi}\frac{\sin\mu r}{\mu r}$ or the integrand of the second term in the expression for $f(\phi)$. We can thus regard the scattering, at least approximately, as caused by a rigid distribution of charge, each element of which scatters a coherent wave of amplitude corresponding to the classical formula. Presumably, when the charge does not scatter as a rigid body we have the case of inelastic collision.

The result can be expressed very neatly by making use of the corresponding X-ray effect. Here the scattering is wholly electronic, that due to the nucleus being negligible. Bragg takes F as the number of electrons which would scatter a wave of the same amplitude as that scattered by the atom. Accordingly F = N if the scattered waves are all in phase, and the ratio F/N measures the mean value of $\frac{\sin\mu r}{\mu r}$ for the electrons in the atom. Hence

$$\frac{e}{2mu^2\sin^2\frac{1}{2}\phi}\int_0^\infty \frac{\sin\mu r}{\mu r}\cdot\sigma dr = \frac{-Fe^2}{2mu^2\sin^2\frac{1}{2}\phi}$$

and

$$f(\phi) = \frac{e^2}{2mu^2\sin^2\frac{1}{2}\phi}(N-F).$$

The original expression for $f(\phi)$ shows that it is a function of $\sin\theta/\lambda$ since $\theta = \frac{1}{2}\phi$. This is in agreement with the experiments on gold. Mott has compared his theory with the experiments, using for F a value calculated for gold on assuming a distribution of charge given by a form-

[1] Compton, *X-rays and Electrons*, (New York, 1926) p. 148.

ula due to Thomas. This method has been found to be satisfactory as a means of calculating F for X-rays.

The extent of the agreement is shown in Figure 42 taken from a letter by Mott.[1] The full line is $\frac{(N-F)\lambda^2}{\sin^2\theta}$ in arbitrary units. The dotted line shows the result of applying a correction for the heat motion of the atoms

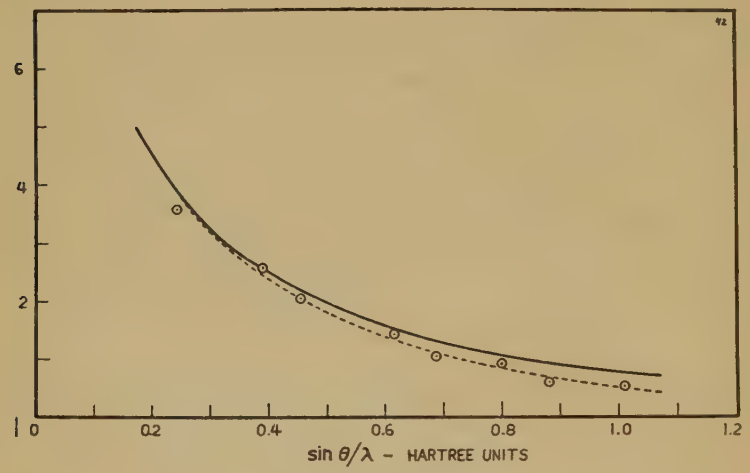


FIG. 42

in the gold crystals. It will be seen that the result is in perfect agreement with the experiments. The scale is chosen so as to fit the experimental points (circles) at $\sin\theta/\lambda = 0.32$.

Mott[2] has also found good agreement with experiments by Dymond on the scattering of electrons in helium. In this case the distribution of the charge in the helium atom was taken as that calculated by Hartree.

[1] Mott, *Nature*, **124**, 986 (Dec. 28, 1929).
[2] Mott, *Proc. Cambridge Phil. Soc.*, **25**, 306 (1929).

CHAPTER VII

Theoretical Interpretation

It is worth while to consider carefully what theoretical deductions may be made from experiments such as those referred to in Chapter VI. A point of importance is the fact that in the writer's transmission experiments there would seldom have been more than one electron in the film at once. Thus, since it is almost inconceivable that an electron outside the film should influence the process of diffraction, one must suppose that each individual electron is treated by the film in such a way as to make it much more likely that the electron will fall on or near a ring than in the regions between.

The results of the transmission experiments may be approximately explained by the following assumptions:

(1) Each electron is associated with a wave of approximate wave-length h/mu, the length of the train being at least 50 waves and the breadth in the wave front at least 30×10^{-8} cm. in certain cases.

(2) Each atom of the crystal is the center of a wavelet coherent with the original wave, and whose intensity varies with the angle to the original direction of motion of the electron, in a manner which can be calculated from the distribution of charge in the atom (p. 115).

(3) The chance of the electron appearing at any place with its original energy is proportional to the intensity of the composite wave formed by the wavelets.

It should be noticed that the electron is detected by any of a number of processes, such as the charging of a Faraday cylinder, the development of the grain of a photographic plate, or a scintillation on a screen, all of which can be interpreted only as the arrival of a particle with a certain charge and energy.

(4) There is also a chance of the electron losing energy in passing through the crystal. In this case its deflection is governed by other laws of which little is known at present.

The discrepancies between the above theory and the reflection experiments at low voltage apparently can be explained by considerations of the type presented at the end of Chapter V, which involve the investigation of the interaction of a wave train with the complicated periodic distribution of potential in the crystal. On this view assumption (2) is a convenient approximation to the result which would be obtained by a rigorous solution of Equation (5), p. 29, using for F the actual distribution of potential throughout the crystal. Mott's calculation of the scattering of single atoms also falls into line with this view.

It seems, then, that we may regard the reflection experiments as accounted for by assumptions (1)–(4) above, if they are modified in the sense that the chance of an electron appearing is to be taken as proportional to the intensity of the scattered waves which satisfy Equation (5), page 29, using a value of F determined by the structures of the crystal and of its component atoms.

It should be emphasized that, at least so far as present knowledge goes, the behavior of any particular electron must be expressed in terms of probability. For example, in a transmission experiment there is no way of knowing in advance whether any given electron will appear in the central spot or on a ring, and the same difficulty would arise even if the crystal were large and there were only one Laue spot to which diffraction could occur. In addition, there is always a probability of inelastic collision. It seems possible, however, at least in theory, to regard each electron as an individual particle fastened in such a way to a wave system obeying Equation (5), page 29, that it always moves along the wave normal. The expression for the necessary velocity has been given in practically equivalent forms by de Broglie[1] and Schrödinger.

[1] L. de Broglie, *J. phys. radium*, 8, 225 (1927).

The following treatment is from Sommerfeld.[1] We have $\frac{\partial\psi}{\partial t} = \frac{h}{4\pi i m}(\nabla^2 - \frac{8\pi^2 m}{h^2}\mathrm{F})\psi$ from Equation (6) page 32. For the conjugate ψ^*: $\frac{\partial\psi^*}{\partial t} = -\frac{h}{4\pi i m}\left(\nabla^2 - \frac{8\pi^2 m}{h^2}\mathrm{F}\right)\psi^*$. Multiply the first equation by ψ^*, the second by ψ and add, thus eliminating F,

$$\frac{\partial}{\partial t}(\psi\psi^*) = \frac{h}{4\pi i m}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*).$$

Now whatever the functions ψ, ψ^*,

$$\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2} = \frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)$$

$$\cdots\cdots\cdots\cdots = \cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots = \cdots\cdots\cdots\cdots$$

Hence

$$\psi^*\nabla^2\psi - \psi\nabla^2\psi^* = \mathrm{div}(\psi^*\mathrm{grad}\psi - \psi\mathrm{grad}\psi^*)$$

and

$$\frac{\partial}{\partial t}(\psi\psi^*) + \frac{h}{4\pi i m}\mathrm{div}(\psi\mathrm{grad}\psi^* - \psi^*\mathrm{grad}\psi) = 0.$$

Schrödinger has shown that the quantity $e(\psi\psi^*)$ behaves like the density of electricity. Hence the above equation may be regarded as expressing that no electricity is created or destroyed, if we take the quantity in parentheses as proportional to a current. We have, in fact, the current density $j = \frac{eh}{4\pi i m}(\psi\mathrm{grad}\psi^* - \psi^*\mathrm{grad}\psi)$. If the density of a continuous distribution of electricity of one sign is ρ and the current is j then the velocity is j/ρ. In the above case this is

$$w = \frac{eh}{4\pi i m}\frac{\psi\mathrm{grad}\psi^* - \psi^*\mathrm{grad}\psi}{e\psi\psi^*} = \frac{-h}{2\pi i m}\mathrm{IM}[\mathrm{grad}\log\psi]$$

where IM signifies "the imaginary part of". Sommerfeld and Schrödinger appear to prefer to deal rather with the above expression for the current than with the velocity, but de Broglie uses an expression equiv-

[1] Sommerfeld, "Atombau und Spectrallinien" in *Wellenmechanische Ergänzungsband*, 105.

alent to the above for w. It should be noticed that if we turn back to Chapter I and substitute for our original wave expression $\psi = a_{xyz} \sin(nt - \phi_{xyz})$ the complex form $\psi = a_{xyz} e^{i(nt-\phi)}$, then

$$\begin{aligned} \text{IM}[\text{grad log}\psi] &= \text{IM}[\text{grad log } a_{xyz} + i \text{ grad}(nt - \phi)] \\ &= -i \text{ grad } \phi. \end{aligned}$$

Thus $w = \dfrac{eh}{2\pi m} \text{ grad } \phi$. The phase velocity $v = \dfrac{n}{\text{grad } \phi} = \dfrac{2\pi mc^2}{h(\text{grad } \phi)} = \dfrac{c^2}{w}$ and $vw = c^2$. This is the extended form of the relation which holds for monochromatic plane waves in the form $Vu = c^2$, where V is the *wave* velocity and u that of the corresponding particle.

So far we have been dealing in differential equations regarded as expressing the behavior of a continuous distribution of electricity. To bring this into line with the experimentally observed discontinuity of electric charge it is usual to reinterpret $\psi\psi^*$ as the probability (per unit volume) of the presence of an electron near an assigned place. The continuity equation then tells us that if we have a dense swarm of electrons distributed according to this law, they will continue to be distributed according to it if they move with the velocity w found above. The swarm indeed need not even be dense, if the state of motion is steady and continues for a sufficiently long time. It follows that all the results of our experiments can be stated in the form, that an electron moves along the normal to a certain wave ψ with velocity w, where ψ is determined as a solution of Equation (4) page 29 (which of course includes (5) as a special case) with the value of F appropriate to the crystal used. This apparently replaces probability by certainty; but the change is apparent only, for we do not know along which wave normal any given electron has started, and normals originally close together may and will ultimately diverge widely. Nevertheless, the above view seems to me helpful in enabling one to form a mental picture of what is taking place. On this view, then, one regards each electron as accompanied by a wave which guides it. The electron is obliged, by the

law of its existence, to move always along the normal to this wave at the speed given by the above expression. The form of the wave is governed by the nature of the expression for F which describes the field in which it moves; thus the presence of an atom will influence the motion of the electron even though the particular wave normal along which the electron is moving may pass the atom at a considerable distance. However, the effect of a distant atom will, in general, be less than that of one near the line of motion. To illustrate this consider electrons incident normally on a plane grating consisting of a rather small number of atoms (Figure 43). The electrons will be

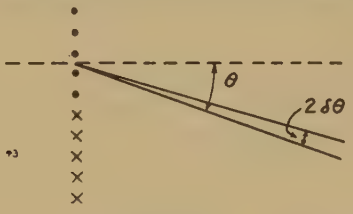


FIG. 43

diffracted, but since the resolving power is limited the diffracted beam will be wide, and the electron may, with about equal probability, be at any angle from $\theta-\delta\theta$ to $\theta+\delta\theta$. The atoms have deflected it through an angle of the order of θ. Now add an equal number of atoms ($\times$ in Fig. 43) at one end of the grating. Apart from a doubling of the intensity (if the electron beam is supposed to extend over the whole of the new grating) the effect of the doubled resolving power is to diminish $\delta\theta$ to $\frac{1}{2}\delta\theta$. We may say that the effect of the added atoms on those electrons which passed through the original part of the grating has been to deflect them through an angle $\frac{1}{2}\delta\theta$, small compared with the angle θ through which they were deflected by the original set of atoms close at hand.

It seems necessary to suppose a separate wave system for each electron, not only because the diffraction takes place under conditions when only one electron is present in the film at a time, but also because it would be perfectly possible to detect the electrons separately and so each must be regarded as an individual. But this view raises

difficulties concerned with the length of the train of waves. A monochromatic train extends to infinity in both directions and is a physical impossibility. It is difficult to see, for example, how the length of an approximately uniform train for an electron in a diffraction experiment could exceed the distance between the cathode and the photographic plate. But if the train is not monochromatic it can be analyzed into Fourier components of different wave-lengths and these waves will have an appreciable intensity over a finite range. To each wave-length corresponds a velocity by the formula $\lambda = h/mu$. Which are we to take as the velocity of the electron?

Without further information the velocity must be regarded as indeterminate, and this view is in agreement with the "uncertainty principle" due to Heisenberg, which has had great influence on physics in the last few years. This principle asserts that between any co-ordinate q of a particle and its canonically conjugate momentum p the relation exists that, if Δq is the uncertainty with which the first can be measured and Δp that for the second, then $\Delta p \Delta q \sim h/2\pi$. This statement, which is strictly true only for a free particle, was originally deduced from a detailed consideration of the errors involved in measurements owing to the interaction of the means of detection (light quantum or electron) with the object to be investigated. On the wave theory it appears as a natural consequence of the above considerations concerning finite wave trains. Thus we can only be perfectly certain of the velocity of an electron when it is associated with an infinite wave train, and then its position is quite indeterminate; for we cannot proceed to determine the position without cutting the train. If the train is of length l, this is the uncertainty of position. The corresponding uncertainty of momentum can be found as follows. Let there be N waves in the train, then the result on page 71 shows that the wave-length ranges from $\lambda - \Delta\lambda$ to $\lambda + \Delta\lambda$, where $N = \lambda/\Delta\lambda$. Hence $\Delta\lambda = \lambda^2/l$. But $\lambda = h/p$, therefore $\Delta p = -\frac{h\Delta\lambda}{\lambda^2} = \frac{-h}{l}$, or $\Delta p \Delta q = h$, the sign having no significance. Here we have assumed a distribution of waves with constant intensity over a range

$\lambda-\Delta\lambda$ to $\lambda+\Delta\lambda$, thus $\Delta\lambda$ is the maximum uncertainty from the mean. The probable error will be less. In the particular case of a distribution of intensity following the error law it can be shown that $\Delta p \Delta q = h/2\pi$. In all cases it will be of this order. Thus we can only determine the momentum of a particle accurately if we have a long train of waves available, which makes the position uncertain, and conversely.

To take a concrete case: let us suppose that a stream of electrons is allowed to enter a chamber through a valve open for only a very short time as in Figure 44.

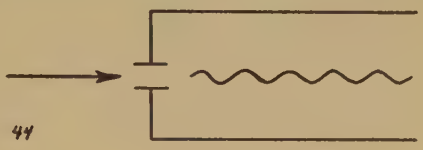


FIG. 44

Such a valve might, for example, consist of a condenser across which a sufficient potential could be placed to drive the electrons to the sides and so exclude them from the vessel. Then the train of waves allowed to enter is of finite length and, however homogeneous the incident beam of electrons, those inside will show a variation in momentum or an "uncertainty", the more pronounced the shorter the time during which the valve was open. By the ordinary view one would attribute this variation to a disturbing force exerted by the mechanism of the valve, but the argument shows that whatever this mechanism may be, there is an irreducible minimum of uncertainty for any given length of wave train.

A similar uncertainty attaches to the position in the wave front, with which is correlated sideways velocity. In fact if we have an infinite plane wave, whose direction can be determined with perfect exactness, the position in the wave front is quite indefinite. By contracting the wave front the position can be made more certain, but the direction then becomes uncertain for the waves will spread by diffraction. If the wave front is reduced to a point the direction becomes completely undetermined. The nature

of the relation between the two uncertainties can easily be seen. If a plane wave of width d be admitted through a slit (Fig. 45) there will be appreciable diffraction up to an angle λ/d on either side. The original momentum was p, the sideways component of the diffracted momentum is thus anything between $\pm\lambda p/d$. But $\lambda = h/p$, so this becomes $\pm h/d$ and the uncertainty of position is $\pm d/2$ in the same sideways direction, so that the product of the two uncertainties for this direction is $h/2$.

Another pair of canonically conjugate quantities are time and energy. Thus if the energy of a system is to be known very exactly the experiment must extend over a considerable time. Suppose the system whose energy is

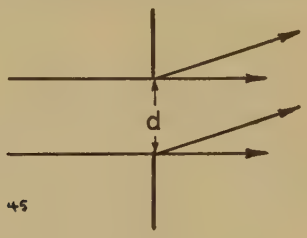


FIG. 45

required is a photo-electron. Its energy will be known if the energy level from which it comes is known and also the frequency of the light which ejected it. [We may suppose the electron to come from a gas molecule in a good vacuum and so get rid of the additional uncertainty caused by collisions.] But if the time is restricted to an interval t there will only be tv waves of light incident on the atom, and the frequency will be uncertain by a fraction of the order $1/tv$ giving an uncertainty of energy $hv/tv = h/t$ and the result follows as before. One cannot say that a given particle has a definite energy at a given time, anymore than one can say that it has a definite frequency. Thus the conservation of energy has no meaning except statistically.

This "uncertainty" principle has been regarded as destroying the basis for the idea of determinism in physics. If the world is subject to an irreducible uncertainty, it is impossible to say that definite effects follow definite causes, because we do not know with sufficient certainty either

the causes or the effects. While this is undoubtedly true, as far as it goes, it may be pointed out that exact laws are not excluded by the fact that they are unverifiable. It seems to be purely a matter of convenience. There is no object in discussing exact laws which cannot be verified, if the inexact laws will explain the observations with convenience; but conversely, there should be no objection to postulating laws and quantities which afford a convenient and graphic mode of expression, merely because they are not observable without introducing uncertainties. Such an objection would apply equally to the introduction of the electric and magnetic vectors as separate quantities in general electrodynamic theory, for the only quantity that can really be observed, viz., the force on a charged particle, is compounded from them. It seems, then, quite legitimate to keep to the idea of a particle moving with definite velocity, even in the case of short wave trains where this velocity cannot be accurately measured. It is of interest to consider what this velocity actually turns out to be. Darwin has investigated a number of cases of the propagation of groups of waves corresponding to free electrons.[1] The simplest case is that of one dimension and no external forces.

Darwin takes the equation $\frac{1}{2}(h/2\pi i)^2 \frac{\partial^2\psi}{\partial x^2} = -\frac{h}{2\pi i}\frac{\partial\psi}{\partial t}$ (the change of sign from our Equation 6, page 32, is merely a change from ψ to ψ^*) and assumes a solution of the type $\psi(x,t) = \int e^{\frac{i2\pi}{h}(px - p^2t/2m)}\phi(p)dp$, where $\phi(p)$ is to be determined to fit the initial conditions. This expression is equivalent to taking the sum of a number of waves corresponding to momenta p. Notice that as the relativity mass is not used the wave velocity, $p/2m$, is quite different from the value given by the general theory. The change is equivalent to taking out the high frequency m_0c^2/h from all the vibrations and, as it were, observing the heterodyne waves instead of the original train. It does not, however, affect questions of wave-length or of the motion of the particles.

[1] C. G. Darwin, *Proc. Roy. Soc. London*, **A117**, 258 (1927).

For the wave at $t=0$ Darwin assumes

$$f(x)=\exp[-\tfrac{1}{2\sigma^2}(x-x_0)^2+i\,\tfrac{2\pi}{h}\,mv(x-x_0)].$$

This is a group centered round $x=x_0$ with an intensity $\rho=e^{-\frac{(x-x_0)^2}{\sigma^2}}$ so that σ represents the uncertainty with which the electron is situated at x_0. The independent quantity v determines the wave-length, but for the moment we will not attribute any other physical significance to it. To determine $\phi(p)$ we have at $t=0$:

$$\int e^{i\frac{2\pi}{h}px}\phi(p)dp=f(x)=\exp[-\tfrac{1}{2\sigma^2}(x-x_0)^2+\frac{i2\pi}{h}mv(x-x_0)]$$

of which the solution is:

$$\phi(p)=\frac{\sigma}{h}\sqrt{2\pi}\exp[-\tfrac{1}{2}\left(\frac{2\pi\sigma}{h}\right)^2(p-mv)^2-\frac{i2\pi}{h}px_0];$$

substitute in the equation for ψ and integrate:

$$\psi(x,t)=\frac{\sigma}{\left(\sigma^2+\frac{iht}{2\pi m}\right)^{\frac{1}{2}}}\exp\left[-\tfrac{1}{2}\frac{(x-x_0-vt)^2}{\sigma^2+\frac{iht}{2\pi m}}+\frac{i2\pi}{h}mv(x-x_0-\tfrac{1}{2}vt)\right]$$

To find the intensity, *i.e.* the probability of an electron at any given place, we multiply by the conjugate and find

$$\rho(x,t)=\frac{\sigma}{[\sigma^2+(ht/2\pi\sigma m)^2]^{\frac{1}{2}}}\exp-\frac{(x-x_0-vt)^2}{\sigma^2+(ht/2\pi\sigma m)^2},$$ thus

the electron at time t is most likely to be at x_0+vt and the uncertainty is $\sqrt{\sigma^2+(ht/2\pi\sigma m)^2}$. We may now regard v as a kind of most probable velocity.

It should be noticed that the use of the imaginary in this work differs from that in ordinary wave theory where we end by taking the real part. Here we are rather concerned, on the one hand with the modulus of the complex quantity which gives us the electric density, and on the other with the argument which gives the velocity. A graph, for example, of the real part of $f(x)$ would have no physical significance. The uncertainty $[\sigma^2+(ht/2\pi\sigma m)^2]^{\frac{1}{2}}$ may be regarded as compounded, by the method of squares, of the two independent uncertainties $\pm\sigma$ and $\pm ht/2\pi\sigma m$; the latter corresponds to an uncertainty $h/2\pi\sigma$ in momentum and the product of this with the uncertainty of initial position is $h/2\pi$, in agreement with Heisenberg.

Now consider the above from the point of view of our definition of velocity:

$$w = \frac{h}{2\pi m}\mathrm{IM}[\mathrm{grad}\log\psi]$$
$$= v + \frac{h^2t}{4\pi^2m^2}\,\frac{x-x_0-vt}{\sigma^4+\frac{h^2t^2}{4\pi^2m^2}}$$
$$= v + \frac{(x-x_0-vt)t}{t^2+\mathrm{T}^2}$$

where $\sigma^2 2\pi m/h = \mathrm{T}$.

If x is the co-ordinate of the electron particle $w = dx/dt$. Let $y = x - vt$, then $dy/dt = \frac{t(y-x_0)}{t^2+\mathrm{T}^2}$ which gives $x = x_0+vt+\mathrm{C}\sqrt{t^2+\mathrm{T}^2}$. The constant of integration C is determined by the initial conditions. If the value of x for the particle at $t = 0$ was really $x = x_0 + \xi$, then the value at any later time is $x = x_0 + \xi\sqrt{1+(t/\mathrm{T})^2}$. Initially the velocity is v in all cases; it then changes and when t is large $x = x_0 + vt + \frac{\xi t}{\mathrm{T}}$, giving a velocity $v + \frac{\xi}{\mathrm{T}}$. This change of the velocity presumably implies a spontaneous change in the energy of the electron, for the energy is regarded as associated with the particle rather than with the waves. At first sight this seems inadmissible, but the whole idea of the uncertainty principle implies an ignoring of the conservation of energy except as a statistical law. Certain facts in connection with the emission of primary β-rays from radio-active substances afford evidence for this view.[1]

It is now generally accepted that the β-rays of the continuous spectrum are primary products of the disintegration of those radio-active substances which emit them, and that each atom in disintegrating gives one β-ray. This has been shown by Gurney[2] for RaB, RaC, ThB and ThC, and by Emeléus[3] for RaE. These β-rays cover a wide range of energy (40,000 to 1,050,000 volts for RaE), and Ellis and Wooster[4] have shown that the total heating effect of the

[1] G. P. Thomson, *Phil. Mag.*, (7) 7, 405 (1929).
[2] Gurney, *Proc. Roy. Soc. London*, **A109**, 540 (1925); *ibid.*, **A112**, 380 (1926).
[3] Emeléus, *Proc. Cambridge Phil. Soc.*, **22**, 400 (1924).
[4] Ellis and Wooster, *Proc. Roy. Soc. London*, **A117**, 109 (1927).

RaE is represented by the kinetic energy of the β-rays determined from their magnetic spectrum. It follows that this represents the original energy distribution, and that no considerable part of the energy is dissipated either before the ray leaves the atom or in internal changes in the atom after the ray has left it. We are thus reduced to suppose: either that the conservation of energy does not apply to each individual process; or that among the atoms either of the RaE or of its product RaF (or both) there are some individuals with a million volts more energy than others; or that there is some way, at present unknown, by which the atoms can equalize their energies.

It seems difficult to believe that this large amount of energy would not affect previous or subsequent rates of transformation. One might expect, for example, that some atoms of RaF which contained an unusually large amount of energy would break up faster than the rest, so that the curve of decay would not be exponential. Actually, of course, RaF (polonium) was one of the cases from which the exponential law was originally deduced.

The difficulty of supposing that the atoms of RaF, as they are formed, can arrive at a state of equipartition with one another is greatly increased by the fact that the individual atoms may be widely spaced with non-radioactive atoms in between. Radiation by quanta in the ordinary way would be absorbed in many cases by these neutral atoms, which presumably could not store it in their nuclei, but would absorb it photo-electrically and ultimately turn it into heat, contrary to the experiment.

We are left with the alternative that the energy is not conserved in each individual act of emission, but only as a statistical average. If the β-ray is regarded at the moment of emission as consisting of a very short wave train, or pulse, the subsequent motion can be analyzed as above. The chief difference is that the wave system presumably has spherical symmetry which, however, does not change the mathematics very much. As before, the initial velocity is always the same, so that the loss of energy by the nucleus is fixed. If the quantity corresponding to ξ, the initial position of the electron particle, is supposed to vary so that

the probability of any value is proportional to $[f(x)]^2$ or ρ, then the final distribution of the momenta will obey an error law about a mean value. This is, in fact, approximately the distribution actually observed, for $N\delta p = N_0 e^{-\frac{(p-p_0)^2}{d^2}} \delta p$ gives roughly the number of β-rays with momenta between p and $p + \delta p$. If the above analysis is right the uncertainty in position in the original pulse will be $\sigma = \frac{h}{2\pi d}$. Now, if the expression for ρ were a physical disturbance it could be analyzed by Fourier series into sine curves, and we can find the wave-length for which the intensity would be a maximum. It is $\pi\sigma$ or $h/2d$. The wave-length of the observed β-rays which gives the maximum number is h/p_0, if the number is plotted on a basis of p. Plotted inversely, on a basis of λ, the wave-length of the maximum of the distribution curve can be shown to be $\frac{2h}{p_0 + \sqrt{p_0^2 + 4d^2}}$. Now calculation shows that, for RaB, ThB and RaE, $\frac{1}{2d} = \frac{2}{p_0 + \sqrt{p_0^2 + 4d^2}}$ within the error of the experiments. This suggests that the distribution of intensity ρ acts like a real physical disturbance of a medium. The wave of the β-ray is like the explosive wave of the firing of a gun, which is a sharp crack near at hand but spreads into a longer train owing to dispersion of intense sound waves; or like the splash produced by dropping a stone into a pond, which at a great distance takes the form of a regular succession of waves with slowly changing wave-length. Indeed, what has been said on page 23 about the analysis of the latter problem in terms of groups applies almost directly to the electron waves.

The irregular disturbance spreads because the groups of which it may be regarded as composed move at different rates. The speed with which it is necessary to move in order to keep always with waves of the same wave-length is the group velocity for this wave-length. This, by the original de Broglie theory, is the speed of the particle u for which $\lambda = h/mu$, thus the particle has, always, a speed

appropriate to the group of waves with which it is for the moment moving. As the waves spread out the particle tends to a fixed velocity and so moves with a certain group of waves. Which group, of the many possible, is chosen must be regarded as determined by the chance of the initial position of the particle with respect to the wave.

Such a train of waves will, in general, contain a very large number of waves. Thus, suppose an electron released initially photo-electrically with a train of say 1000 waves. There is an uncertainty of 0.1 per cent in wave-length and the same in group velocity, thus when the whole has gone say 10 cm. it will have spread over 1 mm., but for an electron of only 150 volts energy this is 10^7 waves. Had the initial train been assumed shorter, the spread would have been still greater. In the above example the 10^7 waves range over a difference of 0.1 per cent in wave-length; if the train had been shorter, though the spread would have been greater, the range of wave-lengths covered would have been greater also. The length of the train with a wave-length within 0.1 per cent of the wave-length corresponding to a 150-volt electron, would have been the same. It should be remembered that the idea of a group comprising an infinitesimal range of wave-lengths is an idealization which, like that of a monochromatic wave, requires in strictness an infinite length of train. Thus the group idea will give useful results only after the waves have spread to such an extent that the apparent wave-length changes relatively slowly along the train.

The above theoretical work, including the equations in Chapter II, does not apply in a magnetic field. In this case the current vector depends not only on ψ but also on the magnetic field. The field acts like a crystalline medium for the electron waves in that the ray, or path of energy, is no longer normal to the wave front. Thus it would be impossible to obtain an expression for the velocity determined only by the wave. This case was considered by de Broglie[1] at an early stage of the theory, but it does not seem worth while to consider it in detail here, for the assumption that the wave can be expressed by a single

[1] L. de Broglie, *Ondes et mouvements* (Paris, 1926), p. 31.

quantity ψ neglects that property of the electron which was expressed as its spin on the orbit theory. Since the spin is intimately connected with the magnetic properties of the electron it is not surprising that some such difficulty as the above should arise. The solution of it involves the use of more complicated expressions for the waves and is discussed in Chapter IX.

PROBLEMS INVOLVING MORE THAN ONE ELECTRON

There are two classes of "many-electron" problems. One which can be treated by representing a stream of electrons as a solution of a wave equation with only three variables; the other in which the wave equation itself must involve $3n$ independent variables, as in the case of a complicated atom. The former method is equivalent to ignoring the mutual action between the electrons or, at most, to representing it by its average effect on the potential. There is no essential difference from the case of one electron. If, indeed, as is commonly done, the initial beam of electrons is represented by a monochromatic wave, this is an idealization even for a single electron; but however the electron was originally produced and whatever its original wave-train, by the time it has gone even a fraction of a millimeter there will be a train of an immense number of waves over which the change in wave-length is quite negligible. The assumption of a monochromatic wave is thus justified for all practical purposes; and if there are many electrons the only difference is an increase in the effective amplitude of the wave, as long as the Coulomb and Ampère forces between the electrons are negligible. Each electron has its own wave system which determines the chance of its being at any assigned place. The assumption of a single wave for the whole beam is merely a convenient way of superposing the essentially independent effects of the separate electrons.

When, however, the importance of the mutual interactions makes it necessary to use a many-dimensioned wave equation, the definition of velocity which we have used so far breaks down. This case occurs especially with the electrons which form part of an atom. In these cases

the conception of velocity loses most of its value as there is no practical means of measuring it, even approximately. Schrödinger has shown, however, that it is possible, even in this case, to devise a consistent definition. Thus, if the density associated with electron σ is defined by

$$\rho_\sigma = \int \ldots \int . \psi . \psi^* \tau_1 \tau_2 \ldots \tau_{\sigma-1} \tau_{\sigma+1} \ldots \tau_N$$

where the quantities τ_1, etc., are the elements of space associated with the various electrons, and if we define a quantity

$$\iota_\sigma = \int \ldots \int \frac{h}{4\pi i m} (\psi \mathrm{grad} \psi^* - \psi^* \mathrm{grad} \psi)_{\tau_1 \tau_2 \ldots \tau_{\sigma-1} \tau_{\sigma+1} \ldots \tau_N}$$

then $\frac{\partial \rho_\sigma}{\partial t} + \mathrm{div}\ \iota_\sigma = 0$. Thus if ρ_σ is regarded as measuring the probability of the presence of the electron, ι_σ / ρ may be taken for its velocity.

CHAPTER VIII

Physical Theory

The view which we have taken, so far, of the waves is to regard them as an expression of the probability of the appearance of an electron at a given place, or alternatively as the law which governs the motion of electrons. While this view appears to afford an adequate explanation of the experiments which we have been discussing, there are two objections which can be raised to it as a final statement. The first is mainly aesthetic and will appeal to different minds with very different force, it is the absence of a physical picture of the waves. One associates a wave with the motion of some object, and apparently nothing moves, or at least not as wave motion. The second is more definite, and may be best expressed, if in somewhat oldfashioned language, by saying that the existing theory tells us nothing of the connection between ether and matter. In more modern terms: Why does an electron ever radiate light quanta? The existing wave theory of spectra has to carry over from classical theory the expression for the radiation from an oscillating doublet. From the wave theory point of view this is a perfectly arbitrary assumption, for there is no obvious connection between an expression of the type $\int\int\int z\psi\bar{\psi}dxdydz$ and the radiation of energy.

Closely connected with the second difficulty is the fact that we now, for the first time, have non-material waves which do not go with the velocity of light in empty space, and whose wave-lengths are the same as those of other waves with quite different properties. For example, electron waves of 30,000 volts energy have a wave-length 0.71×10^{-9} which is that of a hard X-ray of totally different properties.

The question may be summarized: Can these new waves be regarded as in any way analogous to waves of light,

or must they be regarded as waves of a fundamentally different kind; and if the latter, why are they connected with the waves of light in the intimate relation of cause and effect?

Sir J. J. Thomson, in his paper "Beyond the Electron", has put forward a theory which is, so far, the only serious attempt to solve these two difficulties.[1] He points out that the difficulty of assigning a Maxwellian nature to electronic waves, which arises from their slow transmission of energy, is solved by the peculiar properties of a medium containing free charges, such as has been suggested to account for the Heaviside layer which guides wireless waves round the earth. Such a medium has the property of very strong dispersion of waves of different frequencies and Sir J. J. Thomson calls it a "super-dispersive" medium. He supposes that the region round an electron contains large numbers of charges of mass μ charge $-\epsilon$ and an equal number of mass μ' charge $+\epsilon$. The free periods of each individual charge are considered low compared with those of the vibrations of the joint system.

Maxwell's equations for the system are:

$$\frac{1}{c^2}\frac{dX}{dt} + 4\pi\Sigma\epsilon\frac{dx_r}{dt} = \frac{d\gamma}{dy} - \frac{d\beta}{dz}$$

and two others for Y and Z (1)

$$\frac{dX}{dy} - \frac{dY}{dx} = \frac{d\gamma}{dt} \text{ and two others} \qquad (2)$$

while for each individual charge:

$$\mu\frac{d^2x_r}{dt^2} = X\epsilon \qquad (3)$$

ignoring the effect of the magnetic field.

From equations (1), (2), and (3), we get three equations of the type:

$$\frac{d^2X}{dt^2} + p_0{}^2X = c^2\left\{\frac{d^2X}{dx^2} + \frac{d^2X}{dy^2} + \frac{d^2X}{dz^2} - \frac{d}{dx}\left(\frac{dX}{dx} + \frac{dY}{dy} + \frac{dZ}{dz}\right)\right\} \qquad (4)$$

[1] J. J. Thomson, *Phil. Mag.*, (7) 6, 1264ff (1928); *ibidem*, (7) 8, 1073 (1929).

where $p_0^2 = 4\pi c^2\left(\frac{N\epsilon^2}{\mu}+\frac{N\epsilon^2}{\mu'}\right)$, N being the number of charges of each sign per unit volume.

From Equations (4) we have:

$$\frac{d^2}{dt^2}\left(\frac{dX}{dx}+\frac{dY}{dy}+\frac{dZ}{dz}\right)+p_0^2\left(\frac{dX}{dx}+\frac{dY}{dy}+\frac{dZ}{dz}\right)=0 \qquad (5)$$

This equation is of the type $\frac{d^2\psi}{dt^2}+p_0^2\psi=0$ and indicates a vibration of frequency $p_0/2\pi$. This may be regarded as a physical explanation of de Broglie's fundamental postulate of intrinsic vibration.

Consider a disturbance of the form

$$X = A\cos\frac{2\pi}{\lambda}(Vt-z), \quad Y=Z=0;$$

it will satisfy Equations (4) and thus a wave of this type can be propagated, if V and λ satisfy the relation:

$$V^2 = \frac{p_0^2\lambda^2}{4\pi^2}+c^2 \qquad (6)$$

There is thus dispersion, the minimum wave velocity being c. The group velocity $U = V-\lambda\frac{dV}{d\lambda}=\frac{c^2}{V}$, thus $UV=c^2$ and by (6) $c^4=\frac{p_0^2\lambda^2U^2}{4\pi^2}+c^2U^2$. Hence $\frac{\lambda U}{\sqrt{1-U^2/c^2}}=\frac{2\pi c^2}{p_0}$, a constant for the medium. If this constant is taken as h/m_0 and U is interpreted as the velocity of the electron, we have the de Broglie formula $\lambda=\frac{h\sqrt{1-u^2/c^2}}{m_0u}$. The frequency ν of the waves is $\nu=V/\lambda=c^2/\lambda U=\frac{p_0}{2\pi\sqrt{1-U^2/c^2}}$ thus $p_0/2\pi$ is the minimum frequency for the waves. Putting in values of h/m_0 this frequency comes to 1.08×10^{20} which would correspond to a wave-length,

in air, of ordinary Maxwellian waves of 2.7×10^{-10}, well in the γ-ray region. The actual frequency

$$\nu = \frac{p_0}{2\pi\sqrt{1-U^2/c^2}} = \frac{m_0 c^2}{h\sqrt{1-U^2/c^2}} = \frac{mc^2}{h}$$

giving the usual quantum relation.

If $X = A\cos(pt-mz)$ then from Equation (2)

$$\beta = \frac{m}{p} A\cos(pt-mz) = \frac{A}{V}\cos(pt-mz).$$

The electrostatic energy per unit volume in the wave is $\frac{A^2}{8\pi c^2}\cos^2(pt-mz)$, the magnetic is $\frac{\beta^2}{8\pi} = \frac{A^2}{8\pi V^2}\cos^2(pt-mz)$. Since V is greater than c the mean magnetic energy $A^2/16\pi V^2$ is less than the mean electrostatic, $A^2/16\pi c^2$, and vanishes for very long waves, *i.e.* for the free vibration of frequency $p_0/2\pi$. The difference can be shown to be equal to the mean kinetic energy of the moving particles. Thus the mean value of the total energy per unit volume is $A^2/8\pi c^2$.

The flow of energy can be found from Poynting's vector, in this case $\frac{1}{4\pi} X\beta = \frac{1}{4\pi}\frac{A^2}{V}\cos^2(pt-mz)$, the mean value being $A^2/8\pi V$. But if u is the velocity of the energy this flow must equal u times the mean energy, hence $A^2/8\pi V = uA^2/8\pi c^2$, or $uV = c^2$. Thus we may take c^2/V as the velocity of flow of energy, independently of group considerations and we see at once that it can be made as small as we like, since V increases indefinitely with λ. The problem of the wave transmission of electromagnetic wave energy with the speed of the electron is thus solved, for we naturally take this speed as u. The relation $c^2 = Vu$ can also be arrived at in a manner similar to that used by de Broglie, namely by applying the Lorentz transformation to the free vibration governed by Equation (5).

In the absence of an external field we may write the (one-dimensional) wave equation in the form

$$(-p^2+p_0^2)X = c^2\frac{d^2X}{dz^2},$$

where the factor e^{ipt} has been taken out from X. In his most recent paper Sir J. J. Thomson considers how this equation should be modified in an electric field. He regards this as modifying the distribution of the small free charges or "sub-electrons", so that if N_0 is the value of N when the electron is free from force, N under the action of the force will be given by the equation $N = N_0\left(1+\frac{2eF}{m_0c^2}\right)$ where the potential F is so adjusted that it vanishes when the charged body which causes it is at an infinite distance from the electron. This means writing $p_0^2\left(1+\frac{2Fe}{m_0c^2}\right)$ in place of p_0^2 and the equation becomes:

$$c^2\frac{d^2X}{dz^2}+\left\{p^2-p_0^2\left(1+\frac{2Fe}{m_0c^2}\right)\right\}X=0.$$

This is practically equivalent to Equation (5) of Chapter II if p refers to the frequency of the wave corresponding to the speed u_0 of the electron when F = 0. For in this case

$$p^2=\frac{p_0^2}{1-u_0^2/c^2} \text{ and } \frac{p^2-p_0^2}{c^2}=\frac{u_0^2p_0^2}{c^4}=\frac{4\pi^2m_0^2u_0^2}{h^2}=\frac{8\pi^2m_0}{h^2}E'$$

Further investigation in the case of an electron in a uniform field, shows that the waves spread in such a way that their group velocity at any place is equal to the velocity which the electron would have if it were there. Thus the waves in front go faster than the electron (in group velocity) and those behind slower. Since the group velocity is the velocity of the energy, there will be a separation of energy from the electron, *i.e.* a radiation associated with the acceleration. In the case of the electron in uniform motion the velocity of the energy is, as we have seen, always the same as that of the electron, so that the energy does not escape from the electron.

The region round the electron, through which the distribution of sub-electrons must be supposed to occur, would seem at first sight to be governed by our calculations of the minimum size of the wave system (see page 70). This

would involve a sphere of charge round each electron of many Ångströms in radius. If such were the case, however, the spheres of the various electrons in the crystal would overlap, and the crystal would become a continuous super-dispersive medium. The whole crystal would then be available for transmission of the waves, which is all that is required to give the maximum possible resolving power, except perhaps in the case of surface beams which, however, are usually not very sharp. Thus it is enough to postulate a sphere of sub-electrons for each electron large enough for the collection of them to fill all the space in the solid.

CHAPTER IX

The Magnetic Properties of the Electron

Towards the end of the history of the orbit theory of spectra it became apparent that a simple point electron was inadequate to explain the observed facts. To take only one difficulty, it was found that four quantum numbers had to be assigned to each electron. Now each quantum number may be regarded as fixing one degree of freedom, and a point has only three of these. This and other difficulties were overcome by Goudsmit and Uhlenbeck[1] who suggested that the electron was to be regarded as a spinning body whose axis of spin could vary. Actually it was only necessary to suppose two possible directions for the axis, or rather one direction associated with a spin of either sense. One could think of the axis, for example, as always perpendicular to the orbit and the electron as spinning with or against its orbital motion. Such an electron would be expected to behave like a small magnet, and it was found in fact that agreement with experiment resulted if the moment was taken as $eh/4\pi mc$. This value fits in with the results of the Stern-Gerlach experiments.

Nothing in the preceding theory at all corresponds with this conception of the electron as a magnet to whose axis a definite direction in space is to be assigned, and it is not surprising, therefore, that the theory in this form should fail to account for those facts which made the hypothesis of the spinning electron necessary on the older theory. The necessary extension of the equations to cover this aspect of the electron has been made by Dirac, using the methods of non-commutative algebra; his results have been expressed in more ordinary form and considerably extended by Darwin whose method we shall follow.[2]

[1] Uhlenbeck and Goudsmit, *Nature*, **117**, 264, (Feb. 20, 1926).
[2] C. G. Darwin, *Proc. Roy. Soc. London*, **A118**, 654 (1928); *ibidem*, **A120**, 621 (1928).

The process is essentially a rather tentative one of finding a scheme which shall approximate to that of de Broglie and Schrödinger in the absence of a magnetic field, conform to the relativity principle, and be capable of explaining those results which led to the invention of the spinning electron. It is possible that the scheme suggested may not be final. It is found necessary to substitute for the single wave function ψ of an electron a set of four functions $\psi_1, \psi_2, \psi_3, \psi_4$. These satisfy the group of simultaneous equations:

$$\begin{aligned}
(p_0 + mc)\psi_1 + (p_1 - ip_2)\psi_4 + p_3\psi_3 &= 0 \\
(p_0 + mc)\psi_2 + (p_1 + ip_2)\psi_3 - p_3\psi_4 &= 0 \\
(p_0 - mc)\psi_3 + (p_1 - ip_2)\psi_2 + p_3\psi_1 &= 0 \\
(p_0 - mc)\psi_4 + (p_1 + ip_2)\psi_1 - p_3\psi_2 &= 0
\end{aligned}$$

where c is the velocity of light, $p_0 = \frac{-h}{2\pi i}\frac{1}{c}\frac{\partial}{\partial t} + \frac{e}{c}V$, $p_1 = \frac{h}{2\pi i}\frac{\partial}{\partial x} + \frac{e}{c}A_1$, etc., V being the scalar potential and A_1, A_2, A_3, being the three components of the magnetic vector potential. [This last quantity obeys the equation $\alpha = \frac{\partial A_3}{\partial y} - \frac{\partial A_2}{\partial z}$, $\beta = \frac{\partial A_1}{\partial z} - \frac{\partial A_3}{\partial x}$, $\gamma = \frac{\partial A_2}{\partial x} - \frac{\partial A_1}{\partial y}$, where α,β,γ, is the magnetic force.]

The first principle in dealing with these equations is that ψ_1 and ψ_2 are small compared with ψ_3 and ψ_4. In fact the first approximation leads, as follows, to the old ψ equation in ψ_3 and ψ_4 if there is no magnetic field. In this case $p_1 = \frac{h}{2\pi i}\frac{\partial}{\partial x}$, etc. If ψ_1, ψ_2, are neglected in the last two equations we find[1] $(eV - mc^2)\psi_3 = \frac{h}{2\pi i}\frac{\partial \psi_3}{\partial t}$, thus ψ_3 and ψ_4 vary as $e^{-\frac{i2\pi}{h}(mc^2 - eV)t}$. Hence ψ_1 and ψ_2 will vary as the same exponential and

$$(p_0 + mc)\psi_1 = (mc - \frac{eV}{c} + \frac{eV}{c} + mc)\psi_1 = 2mc\psi_1.$$

[1] The charge on the electron is taken as $-e$, so that $-eV$ is the potential energy. In this chapter m is written for m_0 throughout.

Hence we can take

$$\psi_1 = -\frac{h}{2\pi i}\frac{1}{2mc}\left[\left(\frac{\partial}{\partial x}-\frac{i\partial}{\partial y}\right)\psi_4+\frac{\partial}{\partial z}\psi_3\right]$$

and

$$\psi_2 = -\frac{h}{2\pi i}\frac{1}{2mc}\left[\left(\frac{\partial}{\partial x}+\frac{i\partial}{\partial y}\right)\psi_3-\frac{\partial}{\partial z}\psi_4\right]$$

Substituting in the third equation we get

$$\left(-mc^2+eV-\frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\psi_3=\left(\frac{h}{2\pi i}\right)^2\frac{1}{2m}\nabla^2\psi_3,$$

and the same for ψ_4. This is Equation (6) on page 32 with the addition of the term mc^2, which is merely a rather crude way of taking the internal energy of the electron into account, and is the same approximation to the correct relativity equation that the expression $m_0c^2+\frac{1}{2}m_0v^2$ for the energy is to the exact expression $\frac{m_0c^2}{\sqrt{1-v^2/c^2}}$. The equations thus fulfill the condition of reducing to the old form as an approximation. Darwin has shown that they also satisfy the requirements of relativity.

Darwin also shows that they are related to the electrodynamic potentials by the equations

$$\frac{1}{4\pi}\Box V = e\sum_1^4\psi_\lambda^*\psi_\lambda$$

$$\frac{1}{4\pi}\Box A_1 = -e\{\psi_1^*\psi_4+\psi_2^*\psi_3+\psi_3^*\psi_2+\psi_4^*\psi_1\},$$

and so on,

where $\Box$ signifies $\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}$ and ψ^* is the complex quantity conjugate to ψ.

On analogy with classical electrodynamics we take the electron as equivalent to a density ρ and current density j_1,j_2,j_3, where:

$$\begin{aligned}
\rho &= -e(\psi_1^*\psi_1+\psi_2^*\psi_2+\psi_3^*\psi_3+\psi_4^*\psi_4)\\
j_1 &= ce(\psi_1^*\psi_4+\psi_2^*\psi_3+\psi_3^*\psi_2+\psi_4^*\psi_1)\\
j_2 &= ce(-i\psi_1^*\psi_4+i\psi_2^*\psi_3-i\psi_3^*\psi_2+i\psi_4^*\psi_1)\\
j_3 &= ce(\psi_1^*\psi_3-\psi_2^*\psi_4+\psi_3^*\psi_1-\psi_4^*\psi_2)
\end{aligned}$$

The quantities ρ and j satisfy the equation of continuity $\frac{\partial \rho}{\partial t} + \operatorname{div} j = 0$, as may be verified by the use of the original equations. We thus have a current density expressible entirely in terms of the ψ's and have avoided the difficulty mentioned at the end of Chapter VII that, on the old equations, the motion of the electron was in a direction determined to some extent by the magnetic field and not wholly by the waves. We are not, however, entitled to take j/ρ as the electron velocity, for part of j will be due to the magnetic moment of the electron and only part to its velocity.

For the case of the free motion of the electron V and A disappear. Assume as a solution $\psi_\lambda = a_\lambda e^{\frac{i2\pi}{h}(px+qy+rz-Wt)}$ so that the wave normal is in the direction p, q, r and the wave-length is $\frac{h}{\sqrt{p^2+q^2+r^2}}$, on substituting we have a determinant which reduces to $\frac{W^2}{c^2} - m^2c^2 - p^2 - q^2 - r^2 = 0$. This may be regarded as fixing the wave-length for a given frequency $\frac{W}{h}$. We have, in fact, $\lambda = \frac{h}{\left[\frac{W^2}{c^2} - m^2c^2\right]^{\frac{1}{2}}}$. If W is taken as the total energy in accordance with Planck's relation

$$W = \frac{mc^2}{(1-u^2/c^2)^{\frac{1}{2}}},$$

and

$$\lambda = \frac{h}{\left[\frac{m^2c^2}{1-u^2/c^2} - m^2c^2\right]^{\frac{1}{2}}} = \frac{h}{mu/(1-u^2/c^2)^{\frac{1}{2}}}$$

which is de Broglie's formula.

The four quantities a_λ are not all arbitrary. If we choose a_3 and a_4 as the arbitrary complex quantities A and B, we find from the original equations that $a_1 = -\frac{Ar+B(p-iq)}{mc+W/c}$, $a_2 = -\frac{A(p+iq)-Br}{mc+W/c}$. If these are substituted in the expressions for ρ and j we find that both

are proportional to $|A|^2 + |B|^2$ and that j is along p,q,r, the wave normal.

It is noteworthy that *four* quantities are needed to fix the simplest electron wave, two for each of the complex quantities A and B. One of these variables may be taken as the intensity $|A|^2 + |B|^2$, the other three are needed to fix the "polarization". Now, for a light wave of the most general steady type we have elliptical polarization which is defined by two quantities, *e.g.* the direction of the major axis and the eccentricity. The difference is an expression of the fact that the "magnetic moment" of the electron is not necessarily in the wave front as are the vectors of a light wave. Consequently it takes two angles to fix its direction, as against one in the case of light.

To separate the part of the "current" which should be attributed to the magnetic moment from that which is caused by the convection of electricity, Darwin starts from the classical electromagnetic equations. As long as there are no magnetic poles these can be written in the simple form:

$$\frac{1}{c}\frac{\partial \mathrm{E}}{\partial t} + 4\pi j/c = \mathrm{curl}\,\mathrm{H} \qquad \mathrm{div}\,\mathrm{E} = 4\pi\rho,$$

$$-\frac{1}{c}\frac{\partial \mathrm{H}}{\partial t} = \mathrm{curl}\,\mathrm{E} \qquad \mathrm{div}\,\mathrm{H} = 0,$$

where ρ and $j = \rho v$ are the density and the convection current. The effect of introducing magnetic moments is to change H into $\mathrm{B} = \mathrm{H} + 4\pi\mu$ in the last two equations only. Eliminating H from the first equation we have:

$$\frac{1}{c}\frac{\partial \mathrm{E}}{\partial t} + 4\pi\left(\rho\frac{v}{c} + \mathrm{curl}\,\mu\right) = \mathrm{curl}\,\mathrm{B}.$$

At the distant point of observation we need not distinguish between H and B, and so can attribute the effects to a current $j = \rho v + c\,\mathrm{curl}\,\mu$. Thus if part of the current can be attributed to the electron's velocity and part is the curl of a certain vector, the latter can be taken as the magnetic moment of the electron.

By considering the behavior of a "wave packet", like that considered on page 127, Darwin is able to do this ap-

proximately for the case of a slowly moving electron; he finds for the components of μ:

$$\mu_1 = -\psi_3^*\psi_4 - \psi_3\psi_4^*,$$
$$\mu_2 = i\psi_3^*\psi_4 - i\psi_3\psi_4^*,$$
$$\mu_3 = -\psi_3\psi_3^* + \psi_4\psi_4^*,$$

the total moment being $\frac{eh}{4\pi mc}$, as it should be if the amplitude of the wave is chosen to make ρ correspond to the charge on a single electron. In the more general case terms in ψ_1 and ψ_2 have to be added to the above expression, and there is also a vector corresponding to an electric moment. The direction of the magnetic moment is given by the complex ratio of A:B. In fact, if A and B are respectively proportional to $(1-n)$ and $(-l-im)$ the magnetic moment will be along the direction with direction cosines l,m,n. If a unit sphere is drawn round the origin and we project stereographically from the point where the positive z-axis cuts the sphere, the ratio $-B:A$ is a complex quantity whose components are the co-ordinates of the projection of the point in which the magnetic axis cuts the sphere. The plane $z = -1$ is taken as plane of projection.

The above expressions for the magnetic moments are accurate for a system of co-ordinates moving with the electron. An "unpolarized" beam of electrons would be one in which the magnetic axes were distributed at random in this system of co-ordinates. For other systems Darwin shows that the moments will tend towards the equatorial plane of the moving electrons, in a manner recalling the distribution of the lines of force round a classical electron moving at high speeds. The electric moment is found to be always transverse to the motion.

In a later paper Darwin has considered the effect of a "grating" on a beam of electrons. The "grating" is regarded as a periodically variable electric or magnetic potential limited to the vicinity of a plane. He investigates the state of polarization of the beams forming the first-order spectra. For either a purely electric or a purely magnetic grating the effect on the direction of the magnetic

axis is a simple rotation independent of the initial direction of that axis. Thus, if the beam is initially unpolarized with the axes arranged at random in all directions in space, the effect of the diffraction will be a uniform rotation of the axes as of a rigid body, and they will still be distributed at random in space. Hence no polarization will occur. In some cases, where both periodic electric and magnetic fields are present, Darwin finds that some polarization would occur; but it seems very improbable that

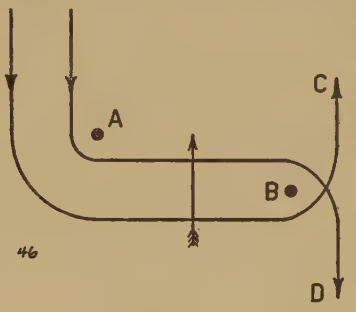


FIG. 46

natural crystal gratings could produce sufficiently strong periodic magnetic fields or that electrons could be gotten near them if they existed, so the result is hardly of practical importance.

In a recent paper Mott[1] has investigated the scattering of a beam of Dirac-Darwin electrons by a fixed nucleus. He finds a kind of polarization after the scattering, which would cause an asymmetry in a second scattering. The asymmetry is not of the type familiar in experiments on polarization of light by reflection, but corresponds to a difference between opposite sides of the beam. Thus, if *A* and *B* in Figure 46 were the nuclei, there would be a difference in the number scattered along *BC* and *BD* corresponding to an asymmetry of the beam between *A* and *B* which can be represented by the arrow. It is not clear why there should be a difference between this case and that considered by Darwin.

[1] Mott, *Proc. Roy. Soc. London*, 124, 425 (1929).

Frenkel[1] has investigated the reflection of Dirac waves at a surface of discontinuity and finds no polarization effect. In view, however, of the short wave-length of the electrons used in most experiments, it seems very doubtful if even the most regular solid surface can be fairly represented as a plane surface of discontinuity.

The whole theory is still incomplete to this extent, that the reaction of its own radiation on the electron is not considered. Consequently the mass of the electron appears as a dynamical quantity in the equations, in contrast to the classical Lorentz electrodynamics where the

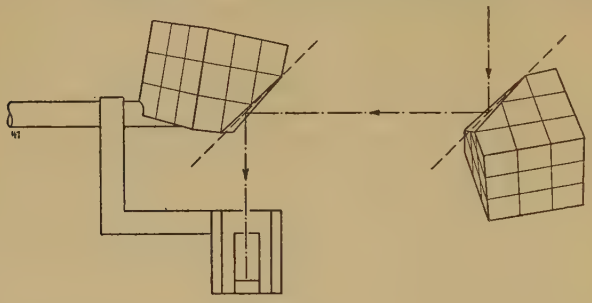


FIG. 47

electronic mass was included in the energy of the electromagnetic field. Also, it is not yet possible to perform any calculation analogous to that which gives the variable electric mass in the case of the classical electron.

EXPERIMENTS

Various attempts have been made to detect, in an electron beam, a property more or less analogous to polarization in light and X-rays. So far none has definitely given a positive result; but in view of the importance of the question, and the uncertainty which there seems to be in the theory, it is worth describing carefully just what has been tried.

Davisson and Germer[2] have made a very careful series of experiments with an apparatus which is analogous to the familiar Nörrenberg mirror experiment in optics. The arrangement is shown diagrammatically in Figure 47.

[1] J. Frenkel, *Compt. rend.*, 188, 153 (1929).
[2] Davisson and Germer, *Phys. Rev.*, 33, 760 (1929).

Electrons are reflected successively from the (111) faces of two nickel crystals at 45° incidence; the second crystal and the collector can rotate as a rigid body about the line joining the two crystals. The voltage of the rays was adjusted until it corresponded to one of the series of values which give selective reflection, and the magnitude of the twice-reflected beam measured for a series of values of θ, the angle determining the position of the collector. In the position drawn in Figure 47 where the twice-reflected beam is in the same direction as the original beam, θ is taken as zero, with the final beam in the opposite direction $\theta = 180°$. For optical reflection the intensity of the second reflection $I = I_0(1+p\cos 2\theta)$ where p is a coefficient which measures the polarization. The observers find that p is less than 0.005 and is zero within the probable error. Mott's theory, however, would suggest a difference between the reflections at 0° and 180°, and there is some slight evidence for this, the values of the deflections being:

θ	*Observations*	*Deflection*
0°	26	3.023±0.026
90°	31	3.057±0.022
180°	31	3.116±0.027
270°	36	3.104±0.022

It seems doubtful, however, if this is really to be regarded as a confirmation of Mott's theory, for any instrumental asymmetry would produce an effect of this kind. The current from the "electron gun" was of the order 2×10^{-4} amp., while that of the twice-reflected current was 10^{-11} to 10^{-12} amp.; it was afterwards magnified about 2 000 times with a vacuum tube amplifier.

Cox, McIlwraith and Kurrelmeyer[1] have carried out a similar experiment but with a polycrystalline gold target instead of single crystals, and β-rays instead of slow electrons. They detected the rays in a Geiger counter. A polarization effect of the nature to be expected from the optical analogy appeared, but was attributed to the disturbing effect of γ-rays. A slight difference was observed between the beams at 90° and 270°. The experiments were

[1] Cox, McIlwraith and Kurrelmeyer, *Proc. Nat. Acad. Sci.*, 14, 544 (1928).

continued by Chase[1] who used lead targets and modified the apparatus to diminish the γ-ray effect. In these experiments the energy of the rays was not, of course, specially adjusted and the reflection was not selective. The values found were:

θ	*Relative Count*
0°	1.000
90°	0.977
180°	0.958
270°	0.969

No effect of the kind found by Cox or of the optical kind is present, but there is a slight effect of the kind predicted by Mott, though in the opposite sense to that found by Davisson and Germer. Chase is inclined to ascribe the effect to a slightly freer path of the electrons in the 0° position.

Joffé and Arsenieva[2] found no effect with a double-reflection apparatus at angles of incidence of 10° and 30°. The mirrors were steel, brass, and glass; but it is not explained how the experiments were conducted with an insulator. Electron energies varied from 80 to 6,400 volts.

The influence of a magnetic field has been studied by Fr. Wolf.[3] On the analogy of the Stern-Gerlach experiment, it might be expected that electrons in a magnetic field besides being deflected would be oriented with their axes parallel and anti-parallel to the field. If they were then reflected, the reflection coefficient might depend on the angle between the field and the plane of incidence. A beam of electrons was bent in a magnetic field, and incidentally rendered homogeneous, by passing through slits. It then fell at 45° on the target, which could be turned so as to vary the plane of incidence but keep the angle constant. The ratio of the electrons retained by the target to those of the total incident beam, showed no perceptible variation with the rotation. The targets were brass, a galena crystal, and a single crystal of copper. The energy of the electrons was about 10,000 volts.

[1] Chase, *Phys. Rev.*, **34**, 1069 (1929).
[2] Joffé and Arsenieva, *Compt. rend.*, **188**, 152 (1929).
[3] Fr. Wolf, *Z. Physik*, **52**, 314 (1928).

Rupp[1] has combined these two types of experiment by finding the effect of a magnetic field applied between the two reflections. The reflecting surfaces were single copper crystals cut along a (111) face. With no magnetic field he found no periodic effects, when sufficient care was taken to make the apparatus symmetrical. The magnetic field used was the horizontal component of the earth's field, the vertical being compensated. No periodic variations were found either with the field along the path of the rays or with it perpendicular to them. The irregular variations varied from about 1 per cent for 380-volt electrons to 5 or 6 per cent for those of 120 volts. In the above experiments the voltage was not adjusted to give selective reflection, though the electrons which had lost energy were rejected by a reverse field. An experiment at 12° glancing angle, with electrons of voltage (150) adjusted to give selective reflection, appeared to show a positive effect; but Rupp is inclined to attribute this to experimental errors due to the very weak currents used.

An entirely different method has been tried by Myers and Cox.[2] They passed a beam of β-rays normally through two sheets of iron foil 0.0025 cm. thick. The foils were magnetized in their own planes, and the direction of magnetization of either could be rotated. Counts were made of the number of β-particles transmitted when the axes of magnetization of the two sheets were parallel, anti-parallel and transverse; but the differences observed were within the probable error. This experiment is, in some ways, analogous to the optical experiment of transmission through two plates of tourmaline.

[1] E. Rupp, *Z. Physik*, **53**, 548 (1929).
[2] Myers and Cox, *Phys. Rev.*, **34**, 106 (1929).

CHAPTER X

Applications of Electron Diffraction

STUDY OF GAS FILMS

The diffraction beams due to slow electrons of a few hundred volts energy are extremely sensitive to the gas conditions. Thus, even with the very high vacuum obtained by Davisson and Germer, a further heating of the crystal by electronic bombardment sometime after the apparatus had been sealed off resulted in a marked improvement in the strength of the beams. Though the necessity of removing the gas from the surface is a disadvantage of the use of slow electrons from one point of view, from another the extreme sensitiveness to gas layers of the diffraction of slow electrons is valuable as affording a means for the investigation of these layers.

Davisson and Germer[1] found that the first effect of heating the crystal was a *reduction* in intensity of all the beams. This reduction lasted only while the crystal was hot and is presumably analogous to the corresponding reduction of intensity of X-ray diffraction by heating, which is due to the disturbance of the regularity of the crystalline arrangement by the heat motion of the atoms. When the crystal had cooled, most of the beams were increased in intensity and the plane-grating beams at grazing incidence, page 52, made their appearance for the first time. These beams are extremely sensitive to gas and slowly disappear as the gas gradually re-forms on the crystal. This effect is shown in Figure 48 (points indicated by circles). The time involved depends greatly on the vacuum conditions; under the most favorable circumstances the changes went more than 20 times as slowly as shown in the figure, under the worst conditions they were so rapid that the plane-grating beams could not be observed. Davisson and Germer attribute these beams to the action

[1] Davisson and Germer, *Phys. Rev.*, 30, 705 (1927).

of the top layer of atoms, and consider that they become quite weak with only a monomolecular layer of gas on the surface. The temperature required to clean the surface is only about 900°, which is a good deal less than would be expected from the results of thermionic experiments. I understand from a conversation that, in some recent experiments with a different nickel crystal, the plane-grating beams failed to appear even after prolonged heating under the best vacuum conditions. The reason is not known.

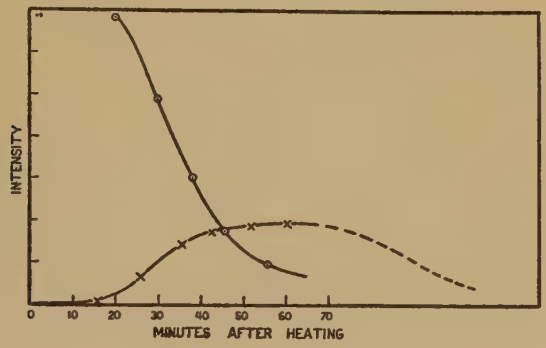


FIG. 48

There is one set of beams in each of the principal azimuths which is permanently destroyed by heating, though it can be restored by releasing a quantity of gas from the charcoal. The beams all attain their maximum intensity at an angle close to 58° from the normal at an energy of 110 volts. They are presumed to be due to a considerable layer of gas and have the character of "space" beams, but it has not been possible to assign a definite structure to the layer.

Another group of beams is more amenable. These show an increase to a maximum after heating, followed by a decrease (Figure 48, points indicated by crosses), and it is natural to ascribe them to a monomolecular layer of gas which would gradually form and then in turn get covered by more gas. At the same time the space-grating beams gradually weaken, but the change is slight even when the new beams have entirely disappeared and it may take

weeks for the space-grating beams to diminish to their original intensity. Under poorer vacuum conditions the whole change may occur in a few minutes. The new beams vary in position over a considerable range as the wave-length changes, without very great change in intensity. They thus possess the character of plane- rather than space-grating beams. Measurement shows, however, that the plane-grating spacing to which they correspond is in

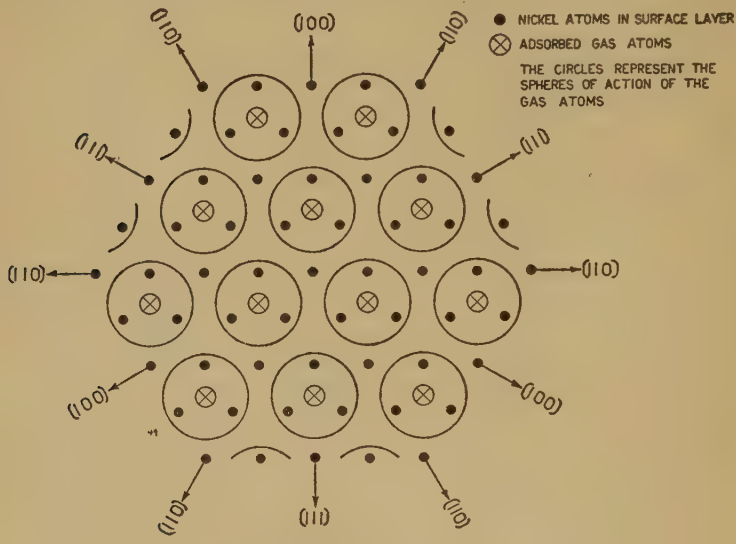


FIG. 49

each case exactly *half* that of the nickel atoms in the azimuth in question. The assumed distribution of the gas atoms (or molecules) is shown in Figure 49. It clearly fulfills the condition that the spacing of the lines of gas atoms perpendicular to any azimuth is half that of the nickel ones. Though mainly a surface effect, the fact that these beams do show weak maxima for certain wave-lengths shows that another layer must come into action to some extent. Davisson and Germer point out that the presence of the gas atoms divides the nickel atoms of the top layer into two classes which are differently shielded from the electrons by the gas. There is, thus, a possibility of their combining with the gas atoms to give an effect

corresponding to the half-spacing. From the voltages at which the beams are strongest Germer estimates the distance of the gas layer from the nickel at 3Å, but this is necessarily subject to considerable probable error.

An interesting peculiarity of these beams is that they disappear at a temperature of 150° though this does not appreciably affect the appearance of the plane-grating beams from nickel. Germer suggests that at this temperature the two-dimensional gas crystal has "melted" and lost its regular arrangement.

Rupp[1] also has studied the formation of gas films on the surface of nickel. He used reflection from a (111) face of a nickel crystal, and measured the variation in intensity of the specularly reflected beam as the voltage of the incident electrons was changed. He found the usual series of maxima when the nickel surface was clean. Addition of hydrogen at 10^{-5} mm. pressure for a short time, caused the appearance of secondary maxima midway between the original ones. This indicates the formation of a structure with half the spacing of ordinary nickel. These maxima may correspond to the "space" beams found by Davisson and Germer. A similar effect was caused by the addition of nitrogen, which Rupp attributes to the nitrogen containing hydrogen as impurity. The addition of hydrogen to the clean surface at the higher pressure of 10^{-3} mm. destroys the maxima, perhaps because of the formation of a thick layer on the surface. The addition of nitrogen after hydrogen destroys the secondary maxima caused by the hydrogen, which Rupp attributes to a chemical action between the gases catalyzed by the nickel. The nickel maxima are also reduced in intensity. If the gases are added in the reverse order the secondary maxima caused by the nitrogen are unaltered. The action of oxygen, hydrogen sulphide or water vapor on the clean nickel destroyed all the maxima, except in one case when the maxima were broadened on the low-voltage side by the addition of hydrogen sulphide. This may be due to the formation of nickel sulphide. Some experiments with the (110) face of an iron crystal gave rather similar results.

[1] Rupp, *Z. Elektrochem.*, **35**, 586 (1929).

STUDY OF SOLID FILMS

During my stay at Cornell University I have attempted to develop the photographic technique of electron diffraction as a means of investigating surface layers, particularly those caused by chemical changes at the surface of a solid. The apparatus used was designed and made at Aberdeen and some preliminary tests and measurements were made there before taking it to America.

The apparatus consists essentially of three parts shown diagrammatically in Figure 50. The first part, *A*, is a discharge tube, operated by an induction coil with rectifying

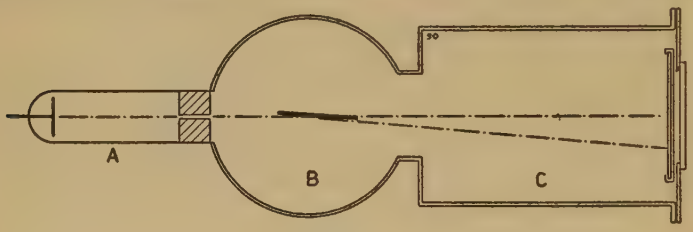


FIG. 50

valve and condenser to steady the discharge. The cathode rays pass through a fine tube into the chamber *B* where they strike the target to be examined. This may be a transparent film or a bunch of fibers set in the beam of the rays, but usually is a flat solid surface from which the electrons are reflected. By means of a somewhat elaborate mechanism three independent motions can be given to the target without disturbing the vacuum. It can be moved bodily in the direction AA' (Fig. 51) perpendicular to the beam of electrons; it can be rotated about an axis perpendicular to the paper; and finally, it can be rotated in its own plane, *i.e.* about BB'. The first adjustment enables the target to be placed correctly in the beam, which would otherwise be very difficult owing to the smallness of the angle θ (1°–3°). The second adjusts the angle θ; and the third alters the azimuth of the target to the rays, a point of importance when the target is a single crystal.

After reflection from the target the rays pass into the camera *C* (Fig. 50) where they are received on a willemite screen and can be observed visually. For a permanent

record, and to detect faint patterns, a photographic plate can be moved in front of the willemite screen by a rack and pinion device. The whole apparatus is tilted so that the main beam of electrons goes along the direction of the earth's magnetic field. This saves the necessity of outside magnets to guide the beam through the fine tube. Exposures are of the order of 10 seconds.

By the use of high-speed electrons and a photographic method of detection, difficulties of technique are greatly reduced as compared with the slow-speed electrons and electric detection used by Davisson and Germer. Thus the

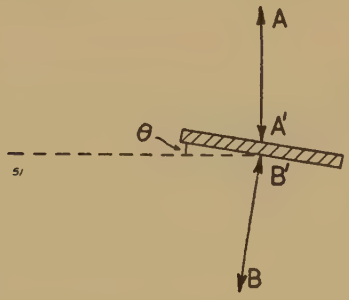


FIG. 51

entire pattern for a given setting is taken at a single exposure in a few seconds, while with electric detection it is necessary to make an exploration in two dimensions to find the beams, if any. In addition, by the use of the willemite screen it is generally possible to tell by inspection whether any diffraction pattern is actually being formed, and one can also make the best setting of the target to give a good pattern. Finally, the use of fast electrons minimizes difficulties due to stray electric and magnetic fields and avoids the necessity of very good vacuum conditions. Against this is to be set the disadvantage that the fast electrons may not be sensitive to extremely thin layers such as monomolecular gas films.

The willemite screen is especially convenient when examining a single crystal. In this case a separate setting of the crystal has, in theory, to be made for each diffracted beam, and it saves plates and time to make measurements

on the screen itself, which can be done with considerable accuracy though not quite so precisely as on a photographic plate.

Polycrystalline Surface Layers

Most of the work done with this apparatus has been done with polycrystalline surface layers giving ring patterns (Figure 53). It is interesting to consider the conditions which must be satisfied before a surface will give a pattern of this kind. In this connection it must be remembered that the angle of incidence is only of the order of 1°.

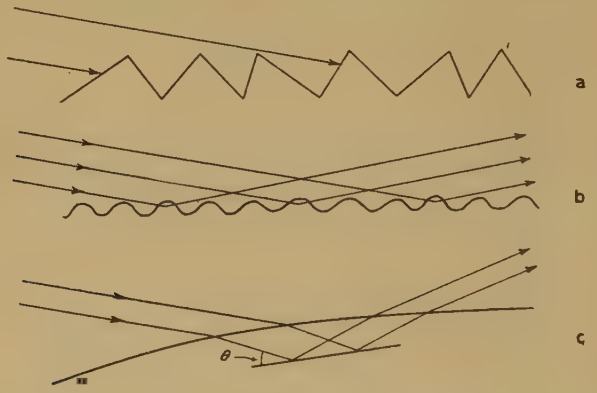
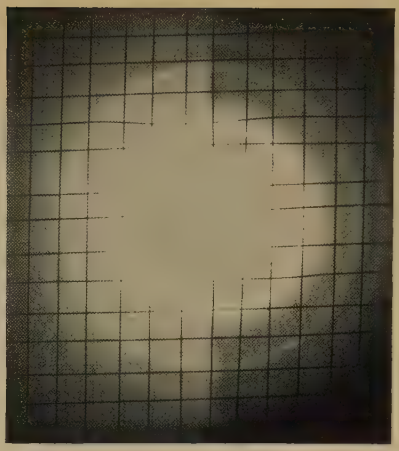


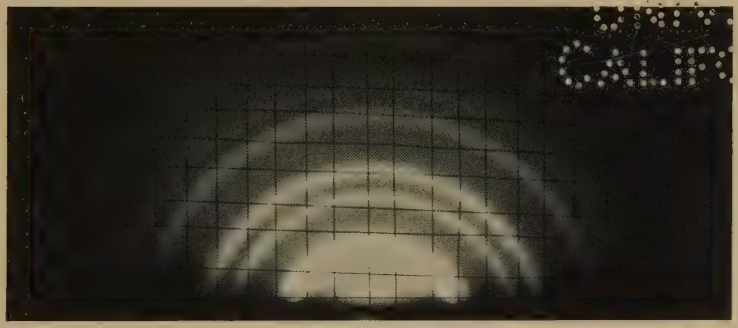
FIG. 52

In the first place, it is obviously necessary that the surface should be crystalline, and this is probably the reason why polished metal surfaces have not shown diffraction rings. The process of polishing presumably produces a layer of amorphous metal, and the electrons are irregularly diffused without forming any pattern. A surface of aluminum etched with caustic potash also failed to give a pattern, this is probably because the etching gives a coarse surface as in Figure 52(a) with facets all making considerable angles with the surface, so that the electrons cannot strike at a small enough angle. A layer of gold spluttered on quartz gives very good rings. The surface is matt and probably consists of a series of irregular lumps small enough for the electrons to penetrate them and be reflected from interior planes (Fig. 52, b). Gold and copper deposited electrolytically do not show rings.

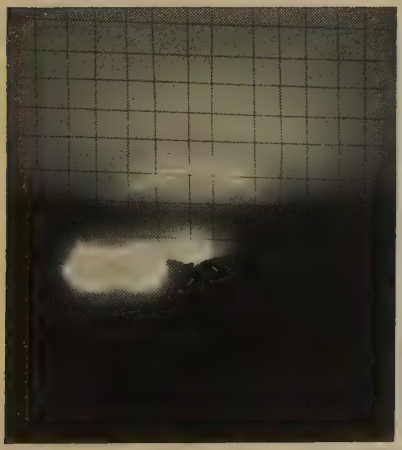
a. Unplatinized Asbestos



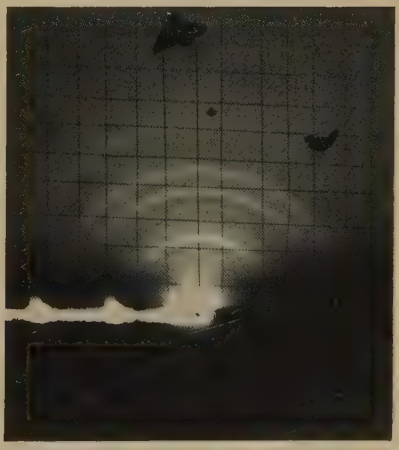
b. Platinized Asbestos



c. Gold spluttered on Quartz



d. Sulphur on Copper



e. Platinum on Copper

FIG. 53

It is possible that in some cases the existence of a refractive index may prevent ring formation. Thus, consider a gently waving surface with a parallel beam of electrons striking it at a small angle (Fig. 52, c). Suppose the refracted beam makes an angle θ with a certain plane which satisfies Bragg's law; the deviation will differ from 2θ because of the refraction at the surfaces, and calculation shows that for equal θ it depends on the angle between the surface and the incident beam. Thus if this angle varies over a degree or two, the rays selectively reflected from the same plane in different parts of the target will be at angles which differ by the amount of the refraction. As we have seen (Chapter V, p. 95) this is comparable with the whole of the deviation, so any pattern which might have been formed will be hopelessly blurred. This effect will occur only when the surface is nearly flat on a scale comparable with the distance of penetration of the electrons. If it is rough to this scale we have the effect illustrated in Figure 52(b) and the electrons will go through the lumps. They penetrate each lump at a considerable angle of incidence and in such a case the deviation due to refraction ($\mu - 1 \sim 10^{-3}$) is negligible. In general I have found that rings are associated with chemical action at the surface of a previously polished surface.

The sensitivity of the method is considerable, thus a polished copper surface exposed to the air for 3/4 hour acquired a layer of tarnish sufficient to give just detectable rings, although its brightness to the eye was not appreciably diminished. On another occasion I had occasion to bombard a gold film with electrons, using as source a filament coated with barium and strontium oxides. The whole was done in the apparatus under vacuum, and when a photograph was taken after the operation it showed a new set of rings, in addition to the gold. After some search it was found that the new rings agreed perfectly with the structure and spacing of BaO, which had apparently been volatilized from the filament onto the gold surface.

A polished lead surface heated to near the melting point showed rings which, though rather faint, were easily measurable and corresponded to the structure assigned to

PbO by X-ray measurements. A series of tests were made on the surface films formed on copper by metals of the sulphur group. All showed fairly good rings. The films were obtained by dipping polished copper in solutions of potassium sulphide, of selenium oxide, and of tellurium oxide, respectively. A number of rings were found in each case, which obviously corresponded to successive small changes due to the change of sulphur to selenium and tellurium. The structure is not that of Cu_2S, which is known.

Some experiments were made on precipitated platinum in various forms. Precipitated on copper it gives very good rings. These do not correspond to the structure of either platinum or copper and perhaps are due to an alloy. It may be mentioned that copper has been found[1] to inhibit the activity of platinum deposited upon it. When deposited on zinc it showed only one faint ring whose size was compatible with the usual crystalline form of platinum. On aluminum the rings were better, and definitely showed the ordinary face-centered cubic structure of platinum. Platinum deposited on aluminum and zinc shows catalytic activity, though not as strongly as when deposited on nickel.[2] Fibers of platinized asbestos, examined in the apparatus, showed a strong ring pattern, but the curious result was found that samples of the same asbestos showed an identical pattern when unplatinized. This is very surprising, for we should expect the platinum to be deposited on the outside of the fibers, and hence show up strongly in the diffraction pattern. There was about 4 per cent of platinum present, enough to show up strongly in a "powder" photograph taken with X-rays. It is also curious that the rings show no sign of a fibrous structure though the fibers were roughly perpendicular to the electron beam.

SINGLE CRYSTALS

Some experiments have also been made with single crystals such as galena (see page 103), calcite and rocksalt. They show brilliant isolated spots on the willemite

[1] Paul and Windisch, *Ber.*, 46, 4010 (1913).
[2] Paul and Windisch, *loc. cit.*

screen, which are generally very sensitive to a slight rotation of the crystal about an axis normal to its reflecting surface, and also to changes in the angle of incidence. Using the (100) face of rock salt I made some measurements of three prominent spots in the plane of symmetry. Treating these as the 8th, 10th and 12th orders (odd orders of course are missing) they gave, for the (100) planes, spacings of

$$5.5 \times 10^{-8} \text{ cm.}$$
$$5.7 \times 10^{-8}$$
$$5.8 \times 10^{-8}$$
$$\text{mean} = 5.67 \times 10^{-8}$$

The spacings given by X-rays is 5.63×10^{-8}, so there is good agreement without assuming any refractive index. There were also spots closer in, which presumably belonged to the lower orders, but it was not possible to measure them. In many cases the spots formed by single crystals show a marked fatigue effect and it is necessary, after a time, to make a fresh setting using a new part of the crystal.

The absence of refractive index in rocksalt confirms one of Rupp's results.[1] He examined sodium chloride, potassium chloride, and potassium bromide by the method of specular reflection with energies of 10–100 volts. He found reflections from (100), (110) and (111) planes in good agreement with the theoretical spacings without refractive index. A peculiar feature, however, on which he does not remark, is that the same crystal face gave maxima corresponding to two or three of these spacings, though it appears that the crystals were single. One must suppose, apparently, that the surfaces—which had been polished—had been broken up so that pieces of crystal lay with different planes in the apparent surface.

[1] Rupp, *Ann. Physik*, 3, 497 (1929).

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